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COLOR CHARACTERIZATION BEFORE AND AFTER LIME TREATMENT

Hardov S. Dugal, et al

Institute of Paper Chemistry

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16. Abstract In general, ~~the~~ lime treatment removed maximum color from the caustic extract and minimum from the neutral sulfite semichemical (NSSC) effluent.

The massive lime treatment was found to remove 73 percent color and 53 percent total organic carbon (TOC) from kraft decker effluent, and 96 percent color and 80 percent TOC from kraft bleach caustic extract. The analysis of the solids from the decker and caustic effluents showed respective reductions of 73 and 59 percent phenolic hydroxyls, 63 and 26 percent sugars, and 51 and 16 percent methoxyls by lime treatment.

The stoichiometric lime treatment was found to remove 79 percent color and 50 percent TOC from kraft decker effluent, and 64 percent color and 30 percent TOC from NSSC effluent. The analysis of the solids from the decker and NSSC effluents showed respective reductions of 76 and 25 percent phenolic hydroxyls, 31 and "negligible" percent sugars, and 42 and 9.7 percent methoxyls by lime treatment.

In the metal ion-lime system the addition of 150-300 ppm $FeCl_3$ with only 300-500 ppm lime removed about 98 percent color from bleach caustic extract. Over 50 percent of the color left by conventional lime treatment process could also be removed by incorporating polyvalent metal ions with lime. However, below 1000 ppm of lime, the sludge obtained settled slowly. More color could be removed by metal ion-lime system than when each was used individually indicating that a "synergistic" effect exists. (EPA)

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COLOR CHARACTERIZATION BEFORE AND AFTER LIME TREATMENT

By

H. S. Dugal
R. M. Leekley
J. W. Swanson

Project S 800853
Program Element 1BB037

Project Officer

Ralph H. Scott
Chief, Paper and Forest Industries
U.S. Environmental Protection Agency
National Environmental Research Center
Corvallis, Oregon 97330

Prepared for

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ABSTRACT

Four effluents from two different sources were studied before and after lime treatment (massive and stoichiometric).

The massive lime treatment process was found to remove 73 percent color and 53 percent total organic carbon (TOC) from kraft decker effluent, and 96 percent color and 80 percent TOC from kraft bleach caustic extract. The analysis of the solids from the decker and caustic effluents showed respective reductions of 73 and 50 percent phenolic hydroxyls, 63 and 26 percent sugars, and 51 and 16 percent methoxyls by lime treatment. Color bodies not removed by lime from the decker effluent had weight average molecular weight (M_w) < 200, higher OH to C-H stretch ratio, higher carboxylate to aromatic ring ratio and seemed to have more pronounced carbonyl groups than the untreated color bodies. Similarly, color bodies not removed from the bleach caustic extract had M_w < 400, contained aliphatic acid-salt systems, pronounced carbonyl groups, lower carboxylate to carbonyl ratio and chromophores which absorb more below 220 nm. In general, the massive lime treatment is more effective on caustic extract than decker effluent.

The stoichiometric lime treatment process was found to remove 79 percent color and 50 percent TOC from kraft decker effluent, and 64 percent color and 30 percent TOC from the NSSC effluent. The analysis of the solids from the decker and NSSC effluents showed respective reductions of 76 and 25 percent phenolic hydroxyls, 31 and "negligible" percent sugars, and 42 and 9.7 percent methoxyls by lime treatment. Color bodies not removed by lime from the decker effluent had M_w < 500, higher OH to C-H stretch ratio, higher carboxylate to aromatic ring ratio and seemed to have more pronounced carbonyl groups than the untreated color bodies. Color bodies not removed by lime from neutral sulfite semichemical (NSSC) effluent had M_w < 300, and showed no detectable differences in character from the untreated color bodies. In general, stoichiometric lime treatment is more effective on decker than NSSC effluents.

LIME TREATMENT WITH METAL IONS

Addition of 150 to 300 ppm $FeCl_3$ with only 300-500 ppm lime removed about 98 percent color from bleach caustic extract. Over 50 percent of the color left by conventional lime treatment processes could also be removed by incorporating polyvalent metal ions with lime. However, below 1000 ppm of lime, the sludge obtained settled slowly. More color could be removed when metal ions were used with lime than when each was used individually indicating that a "synergistic" effect exists.

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SECTION I

CONCLUSIONS

1. No appreciable changes occurred in the color bodies during shipment of mill effluents from their sources to Appleton, Wisconsin.

2. A correlation exists between the absorbance and the color with concentration of color bodies.

3. Color bodies could be stored in the freeze-dried form for longer periods without any appreciable changes.

4. Color bodies of all effluents could be acidified to give acid-insoluble and acid-soluble components.

5. When the "untreated" effluents are acidified, more of the kraft waste color is found in the acid-insoluble rather than the acid-soluble component. However, in the case of NSSC effluent the opposite is demonstrated.

6. When the "lime-treated" effluents are acidified, the kraft Decker and NSSC effluents give more color in the acid-insoluble component whereas caustic extract gives more in the acid-soluble component.

7. All acid-insoluble components are of higher molecular weight (M_w) than acid-solubles.

8. Generally, acid-solubles contain higher carboxylate content than acid-insolubles and are more open in structure.

9. Color-to-carbon ratio is generally higher in acid-insolubles than acid solubles.

10. In the case of kraft Decker and caustic extract more of the acid-insoluble color bodies are removed by lime, where in the case of NSSC effluent more acid-solubles are removed.

11. Kraft Decker effluents contain higher methoxyl, and phenolic-hydroxyl content than the caustic extract. However, the NSSC effluents contain the highest concentration of these groups.

12. Color bodies which are not removed by massive or stoichiometric lime treatment seem to have the same characteristics.

13. Color bodies which are not removed by lime generally have low M_w, less ligninlike character, higher carboxylate to aromatic ring ratio and lower color to TOC ratio.

14. The upper removal limit of M_w changes from effluent to effluent.

15. Color bodies not removed by lime have an upper M_w limit from 200-500.

16. Addition of certain polyvalent metal ions with lime seems to greatly improve the effectiveness of the lime treatment process. These metal ions should be added to untreated or lime-treated effluents before lime addition.

17. The metal ions and lime together are more effective color removing agents than either of these alone.

SECTION II

RECOMMENDATIONS

1. Further work is needed to determine the structural differences of the color bodies in order to explain differences in response to lime treatment of different effluents. This would lead to a better understanding of the advantages and weaknesses of the existing lime-treatment process and could point the way to improved means of removing color bodies.

2. Pilot-scale study of a metal ion-lime system should be carried out on mill effluents in order to confirm the laboratory findings, and to establish the cost of the treatment involved.

SECTION III

INTRODUCTION

Approximately 90 percent of the United States' chemical wood pulp is produced by the kraft pulping process. In the kraft or sulfate process, black liquor (the spent cooking liquor) is evaporated and the strong liquor is burned to recover cooking chemicals. However, evaporation of dilute wash liquors is uneconomical, and these traditionally have been discharged to streams. It is a common practice to keep wastes in the holding ponds to reduce stream pollution. In spite of various measures taken to reduce pollution, kraft mill effluents discharged into streams are objectionable in color, and further improvements are needed to reduce the color of these effluents.

The nature of color bodies in kraft mill effluents apparently has not been fully investigated. Presumably, two wastes are believed to be the main sources of color in the effluents; weak black liquor and effluent from the caustic extraction stages in the bleach plant. In addition, some color may form in the holding ponds. The black liquor contains degraded thiolignins, degraded carbohydrates, and small amounts of fatty and resin acids and other extraneous materials. The degraded thiolignins are highly colored and may be an important factor in the color of mill effluents. The bleach plant effluents contain lignins, which have been degraded further by chlorination and oxidation, and smaller amounts of other materials. These lignins also are highly colored.

Since lignin is highly resistant to microbiological degradation, the color passes through the biological treatment processes. The colored effluents make the receiving waters brownish in color and reduce the light penetration in water. This reduction in light intensity affects aquatic plants by reducing photosynthesis and thereby adversely affects the dissolved oxygen content of water.

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LIME TREATMENT PROCESS IN GENERAL

The lime-treatment process, developed by the National Council of the Pulp and Paper Industry for Air and Stream Improvement (NCASI) is reported to be capable of removing 85-95 percent of the color from both bleaching and pulping effluents[1-4]. This process has gone through the pilot-plant stage and at present is being used by several mills[5-7].

Three demonstration grants were approved by EPA (formerly FWPCA) to determine the feasibility of lime precipitation of color bodies from mill effluents on larger scales. One of the grants, made to the International Paper Company at Springhill, Louisiana, involved massive lime treatment of bleach plant effluent and brown stock washer effluent (decker) both separately and in combination. The other two grants involved stoichiometric lime treatment of total mill effluents at the Interstate Paper Corporation, Riceboro, Georgia, and at the Continental Can Company at Hodge, Louisiana.

Although the technology of lime treatment was well developed, conflicting results had been reported with respect to the underlying chemistry of the process. However, recent studies by Dence *et al.*[8] have shown that the removal of colored material from spent caustic extraction liquor with lime is a chemical rather than a physical process and that color removal is dependent on (a) the presence of enolic and phenolic hydroxyl groups and (b) on the molecular weight of solids contained in the liquor. No data on molecular weight distribution were reported.

More recent studies done by Dugal *et al.*[9] on kraft Decker effluents from the Interstate Paper Corporation have shown that the color bodies which are not removed by lime treatment have an apparent weight average molecular weight of less than 400. These color bodies were shown to contain conjugated carboxyl groups, some ligninlike character and were associated with colorless carbon compounds.

THE PROJECT AND REPORT

The present project has been divided into two parts. The first part (or Phase I) of the project has been concerned with the chemical and physical characterization of the color bodies in the mill effluents both before and after lime treatment. Effluents from two different mills were studied.

Section IV of this report deals with the study of effluents from the International Paper Company (IPCO) mill at Springhill, Louisiana which used the massive lime-treatment process. Section V describes the study of the effluent, from the Continental Can Company (CONCO) mill at Hodge, Louisiana, which uses the stoichiometric lime-treatment process.

The second part (or Phase II) of the project has been concerned with the lime treatment of mill effluents in the presence of multivalent ions. The objective of Phase II was to establish conditions for an improved lime-treatment process using small amounts of multivalent ions of other metals in addition to lime. This part of the project is described in Section VI. The manner in which the report is organized is shown in Figure 1.

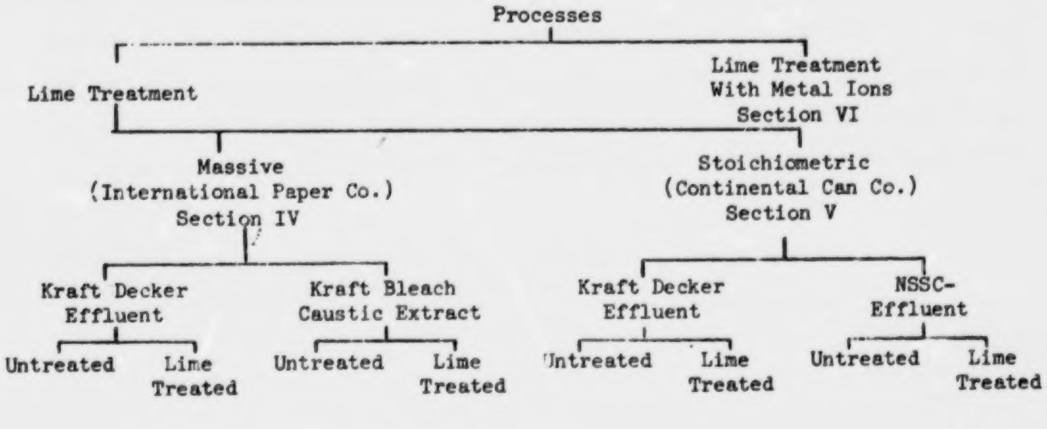
Processes
Lime Treatment
Lime Treatment With Metal Ions Section VI
Massive (International Paper Co.) Section IV
Stoichiometric (Continental Can Co.) Section V
Kraft Decker Effluent
Kraft Bleach Caustic Extract
Kraft Decker Effluent
NSSC-Effluent
Untreated
Lime Treated
Untreated
Lime Treated
Untreated
Lime Treated
Untreated
Lime Treated

Figure 1. Classification of contents of the report

SAMPLING AND HANDLING OF SAMPLES

Composite samples of untreated and lime-treated effluents (containing color bodies that are not removed by lime) were shipped by air from their respective mills to Appleton, Wisconsin. The samples were shipped in five-gallon polyethylene jugs enclosed in especially designed wooden crates provided by The Institute of Paper Chemistry. The usual transit time was two to three days. Previous work[9] had indicated that the color changed upon storage in liquid form, therefore, samples in transit longer than three days were discarded.

A number of samples (including the duplicate ones) were obtained from the mills. Only eight were processed and fractionated according to the program shown in Figure 2 and the rest were investigated in a preliminary way. These eight samples included the decker and caustic extract effluents before and after massive lime treatment, and decker and NSSC effluents before and after stoichiometric lime treatment. The lime-treated effluents which were investigated in detail were obtained from the clarifier before the carbonation stage. Carbonation of these samples was carried out under controlled laboratory conditions. The reason for selecting the lime-treated samples "before" carbonation was that samples carbonated by the mill's stack gases showed an increase in color and TOC values and, therefore, for fear of contamination these were not used for the study. Depending upon the color to TOC ratios and their place in the eluate series of a fractionation run, some fractions were combined to give larger fractions before analysis.

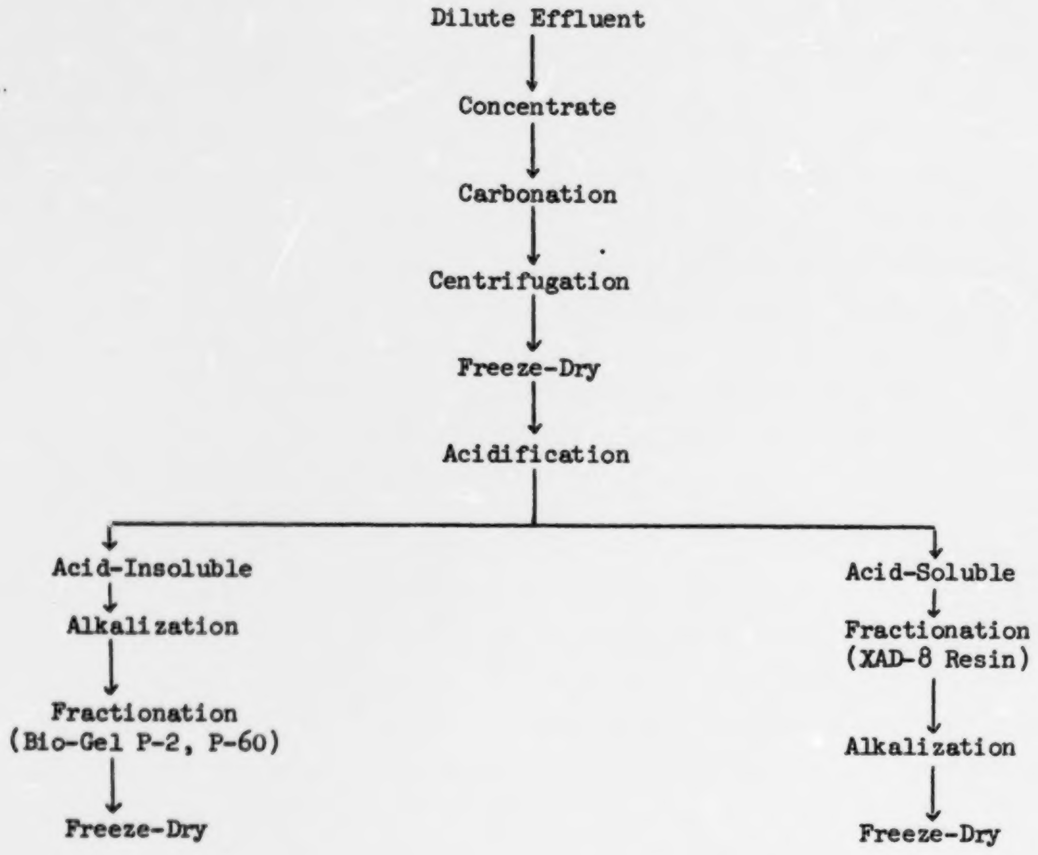
Dilute Effluent
Concentrate
Carbonation
Centrifugation
Freeze-Dry
Acidification
Acid-Insoluble
Alkalization
Fractionation
(Bio-Gel P-2, P-60)
Freeze-Dry
Acid-Soluble
Fractionation
(XAD-8 Resin)
Alkalization
Freeze-Dry

Figure 2. Flow diagram for effluent processing and fractionation

SECTION IV

MASSIVE LIME TREATMENT

(International Paper Company, Springhill, La.)

COLLECTION AND PROCESSING OF EFFLUENT SAMPLES

Source of Effluent

International Paper Company's (IPCO) plant at Springhill, Louisiana is a 1600 ton per day sulfate bleached pulp and paper mill. The mill uses debarked softwood and hardwood chips for pulping. A small percentage of sawdust is also used.

Mill wastes for the massive lime treatment included effluents from the caustic and the unbleached decker stages or a combination of the two. Only a portion of the total effluent (about 25 percent) was treated. This company uses Houghton's antifoaming agent, De Airex 557, for controlling foam problems.

Massive Lime Process at IPCO

The lime treatment system handled 530 gpm of waste and 63 tons of lime (CaO) per day. Lime dosage ranged from 18,000 to 20,000 ppm. The waste and slaked lime were mixed in a 8 x 7 ft reaction tank. The developed floc was allowed to settle in a 26 x 27 ft effluent clarifier. The sludge, containing color bodies, hydrated lime, and fiber, was pumped at 20 percent solids to a 10 x 15 ft lime mud storage tank and after causticizing was burned in a kiln to obtain lime.

The decolorized and clarified effluent that overflowed from the clarifier was treated with 650 cfm carbon dioxide to a pH of 10.5-11.0 in a 30 x 24 ft carbonator. The sludge containing 30 percent solids was sent to the lime kiln and the clear effluent was sent to the impounding basin.

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Color bodies removed from the massive lime process with the sludge are to a large extent soluble in sodium hydroxide. Most of the color compounds dissolve in the white liquor as it is produced in the causticizing process. "White" liquor thus produced with this process is dark in color. Color compounds which remain with lime and are not dissolved in "white" liquor end up in the lime kiln and are burned. Color bodies dissolved in "white" liquor eventually are burned in the mill's chemical recovery furnace.

Variations in the effluent composition did occur because of the fluctuations in the ratios of different kinds of wood used for pulping. Color of the effluent from the caustic stage ranged from 17,000 to 30,000 APHA units. Details of the Massive Lime Treatment Pilot Plant can be obtained from the EPA report[10] based on work done at the IPCO's plant at Springhill, Louisiana.

Effect of Shipment

Four batches of samples, each batch containing the untreated, lime-treated before carbonation and lime-treated after carbonation wastes were received from Springhill, La. over a period of three months. The batches of samples contained effluents from the decker washing stage (referred to as decker), the caustic extraction stage (referred to as caustic), and mixtures containing 75 percent decker-25 percent caustic and 50 percent decker-50 percent caustic.

Chemical analyses on these effluents (before shipment) was supplied by IPCO and are given in Table 1. (Please note the sample code employed as shown in Table 1 footnotes.) Upon receipt at the Institute, representative aliquots of some of the liquid wastes were chemically analyzed and compared with the data of Table 1. The results showed a decrease in color and TOC during shipment. The data fluctuated so much that no definite numbers could be assigned. However, the percentage of color removed, based on data obtained before and after shipment, was almost the same, indicating that the change in color values during shipment is constant and whether this change is real or experimental could not be established.

Table 1. CHEMICAL DATA ON EFFLUENTS BEFORE SHIPMENT FROM IPCO

	100% Decker			75% Decker, 25% Caustic			50% Decker, 50% Caustic			100% Caustic		
ppm	UD8	LTBC8	LTAC8	UDC7	LTBC7	LTAC7	UDC9	LTBC9	LTAC9	UC10	LTBC10	LTAC10
pH value	10.1	12.1	11.7	10.5	13.2	12.6	9.8	12.3	10.7	9.3	12.0	10.5
Total solids	2250	3070	1330	2598	3232	3495	3950	4040	2740	5350	4490	4350
Ash[a]	1260	1700	690	1352	2495	2595	2170	2760	1710	2960	3200	2770
Volatile solids[b]	990	1370	640	1245	737	900	1780	1280	1030	2390	1290	1580
Calcium as Ca	15	504	67	27	466	104	36	536	252	38	552	240
Chlorides as Cl	50	40	35	339	339	339	835	745	724	986	956	986
Color units[c]	890	240	270	5100	215	350	10,500	700	1000	17,000	675	780
Total carbon	260	190	230	475	150	160	1200	280	460	1475	270	430
Inorganic carbon	20	10	10	50	20	20	100	50	40	150	10	150
TOC	240	113[d]	156[d]	425	130	140	1100	230	420	1325	260	280
COD	654	422	462	1437	441	371	2002	478	516	1527	563	572
BOD	192	276	252	246	165	201	252	138	130	192	168	132

[a] Ashed at 600°C for 1 hour.
[b] Calculated by difference.
[c] APHA-color, Pt-Co units.
[d] Calculated figures based on information from IPCO.

UD = Untreated decker effluent.
UC = Untreated caustic effluent.
UDC = Untreated effluent containing UD and UC.
LTBC = Lime-treated before carbonation.
LTAC = Lime-treated after carbonation.
TOC = Total Organic Carbon.
COD = Chemical Oxygen Demand.
BOD = Biochemical Oxygen Demand.
IPCO = International Paper Company, Springhill, Louisiana.
7,8,9,10 = Batch numbers of the respective effluent samples.

Table 1 shows that parameters generally increase with increasing amounts of caustic waste. BOD values appear to be an exception in that they fluctuate but show a downward trend. The results show that caustic extract is about 20 times more colored than the decker effluent. The data further indicate that the color and TOC of lime-treated samples increase after carbonation.

Effect of Freeze Drying and Storage

The liquid samples were first concentrated to one-tenth their volume, carbonated to a pH of 10.2, centrifuged until clear and freeze-dried (see Figure 2). Freeze-dried material was readily soluble in water. Freeze drying of the colored wastes was found to prevent appreciable changes in color bodies during storage.

The effect of freeze drying on color bodies was determined by observing changes in the sedimentation coefficient values of the color bodies before and after freeze drying. The sedimentation coefficient is defined as the velocity of sedimenting molecule per unit field and is a function of the anhydrous molecular weight of the sedimenting substance and the partial specific volume of the solute. It decreases with the decrease in molecular weight and increase in the hydration of the sedimenting molecule.

The sedimentation coefficients were determined according to the method described by Schachman[11] using the ultracentrifuge. The lapse time between the measurements of samples before and after freeze drying was 4-5 days. Results are given in Table 2.

Table 2. SEDIMENTATION COEFFICIENTS OF THE COLOR BODIES

Effluent	Sedimentation coefficients, S[a] Before freeze-drying	After freeze-drying
Untreated decker	1.2	1.2
Untreated caustic	2.0	2.4

[a] S = Svedberg = 1 × 10^{-13}.

Table 3. CHEMICAL DATA ON FREEZE-DRIED WASTES FROM IPCO

	100% Decker			75% Decker, 25% Caustic			50% Decker, 50% Caustic			100% Caustic		
	UD8	LTBC8	LTAC8	UDC7	LTBC7	LTAC7	UDC9	LTBC9	LTAC9	UC10	LTBC10	LTAC10
Yield, o.d. g/100 ml	0.12	0.22	0.25	0.24	0.27	0.26	0.39	0.35	0.30	0.52	0.33	0.34
Ash[a], %	81.5	91.5	89.5	72.8	91.9	90.3	69.1	89.8	90.9	62.2	91.8	90.5
Volatile[b], %	18.5	8.5	10.5	27.2	8.1	9.7	30.9	10.2	9.1	37.8	8.2	9.5
Sulfated ash[a], %	93.8	122.6	113.8	85.6	126.6	122.6	81.3	127.0	126.2	77.3	127.5	115.3
Sodium, %	26.8	34.9	34.3	22.9	33.7	35.1	30.6	37.7	39.8	21.6	33.8	34.9
Calcium, %	<0.10	<0.10	<0.10	0.46	<0.10	<0.10	0.12	<0.10	<0.10	0.15	<0.10	<0.10
Chloride, %	6.3	3.9	4.0	16.7	13.6	13.5	24.7	22.4	22.5	25.5	27.9	27.1
Sulfate, %	34.6	17.2	19.8	17.1	10.2	10.8	5.8	7.7	8.6	1.5	2.9	3.4
Sulfide, %	<0.004	ND	ND	<0.001	ND	ND	<0.004	ND	ND	<0.004	ND	ND
TOC, %	11.4	5.0	5.5	17.6	3.9	3.7	18.5	5.0	5.3	21.2	4.7	5.4

[a] Ashed at 600°C for 1 hour.

[b] Calculated by difference.

For sample code see Table 1.

Table 4. EMISSION SPECTROSCOPIC ANALYSIS OF FREEZE-DRIED WASTES FROM IPCO
(All values on o.d. ash)

	100% Decker			75% Decker, 25% Caustic			50% Decker, 50% Caustic			100% Caustic		
Metals, %	UD8	LTBC8	LTAC8	UDC7	LTBC7	LTAC7	UDC9	LTBC9	LTAC9	UC10	LTBC10	LTAC10
Aluminum	0.430	0.074	0.200	0.240	0.053	0.200	0.110	<0.030	0.084	0.084	<0.030	0.092
Boron	0.016	0.0084	0.0085	0.0068	0.0038	0.0058	<0.004	<0.004	<0.004	<0.004	<0.004	<0.004
Calcium	0.066	0.093	0.098	0.800	0.038	0.046	0.220	0.053	0.045	0.340	0.044	0.054
Copper	0.0016	0.0005	0.0005	0.0008	0.0005	0.0004	0.0007	0.0008	0.0008	0.0012	0.0006	0.0007
Magnesium	0.027	<0.020	<0.020	0.050	<0.020	<0.020	0.089	<0.02	<0.02	0.14	<0.02	<0.02
Manganese	0.0032	<0.001	<0.001	0.0084	<0.001	<0.001	0.006	<0.001	0.0018	0.022	<0.001	<0.001
Silicon	0.070	<0.050	<0.050	0.052	<0.050	<0.050	0.100	<0.050	0.061	0.240	<0.050	<0.050
Sodium	31.0	34.0	33.2	36.7	33.6	32.6	35.8	39.4	33.4	38.7	30.8	34.6
Total[a]	0.614	0.247	0.378	1.158	0.166	0.323	0.530	0.149	0.217	0.831	0.150	0.222

[a] Does not include sodium values.

For sample code see Table 1.

Because no significant changes were noticed in the sedimentation coefficients of color bodies on freeze drying and no appreciable color change was noticed on storage in the freeze-dried state, all color bodies were, therefore, freeze-dried and stored until used for further study.

INITIAL CHARACTERIZATION OF COLOR BODIES FROM THE KRAFT DECKER AND KRAFT BLEACH CAUSTIC EXTRACT EFFLUENTS FROM IPCO

Chemical Characterization

Chemical analysis of the freeze dried wastes is given in Table 3. The results are tabulated according to the increasing amount of caustic extract in the effluent and not according to the batch number. A comparison of all untreated samples shows that as the amount of caustic extract increases the volatile and chloride contents increase whereas ash and sulfate decrease. No particular trend is noticeable in the case of sodium and calcium (calcium was removed by carbonation of mill effluents in our laboratory during processing). The sulfate and chloride removal by lime decreases with increasing amounts of caustic extract.

The ash was analyzed by emission spectroscopy and the results are given in Table 4. The reason for this analysis was to determine whether or not enough metals are present in the system which could form colored complexes with the color bodies. The total amounts of metals in these wastes were very small. Sodium values by the emission spectroscopy method are not as accurate as by the flame photometry method (Table 3) and are not included in the total. Surprisingly enough, no determinable amounts of iron were found in these wastes. The data in Table 4 show that with the increasing amounts of caustic extract in mill effluent, silicon and magnesium increase whereas aluminum and boron decrease. Copper content does not show any definite trend. The data further show that more than 50 percent of the total metals are removed during the lime treatment. However, the ratio of metal content to TOC does not change much indicating that these may be associated with the organic carbon in the effluents (Table 5).

Table 5. CHANGE IN METAL/TOC RATIO DURING LIME TREATMENT OF MILL WASTES FROM IPCO

Effluent	Ratio, metal content/TOC Untreated	 Lime treated[a]
100% Decker	0.04	0.05
75% Decker, 25% caustic	0.05	0.04
50% Decker, 50% caustic	0.02	0.03
100% Caustic	0.02	0.03

All values based on o.d. total solids.

[a] Lime treated before carbonation effluent. (Carbonation was carried out in laboratory under controlled conditions.)

Spectrophotometric Examination

The freeze-dried untreated and lime-treated decker, caustic extract and mixed effluents were dissolved in distilled water to give desired concentrations. Visible and ultraviolet spectra of these aqueous solutions were determined at two pH levels. In one case the pH was "unadjusted" and ranged from 9-10.5. In the other case it was adjusted with a buffer solution to 7.6. Distilled water was used as a reference for all of the samples. Absorbance values of all samples at pH 7.6 were lower than their respective unadjusted samples.

In order to have a reasonable comparative picture, absorptivities at pH 7.6 were calculated from these spectra at different wavelengths by dividing the absorbance values with the volatile solid concentration in g/l. The results are given in Tables 6 and 7 and are plotted in Figures 3, 4, 5, and 6, and compared with those for Indulin-C. Values for LTBC wastes are used. LTAC values fluctuated, probably because of the contaminated stack carbon dioxide which was used for carbonation at the mill site.

Table 6. ABSORPTIVITY[a] VALUES OBTAINED FROM VISIBLE SPECTRUM AT pH 7.6 OF WASTES FROM IPCO

	100% Decker			75% Decker, 25% Caustic			50% Decker, 50% Caustic			100% Caustic			
	UD8	LTBC8	LTAC8	UDC7	LTBC7	LTAC7	UDC9	LTBC9	LTAC9	UC10	LTBC10	LTAC10	Indulin-C
Total solids, g/l	0.4	1.0	1.0	0.4	1.0	1.0	0.4	1.0	1.0	0.4	1.0	1.0	0.175
Volatile solids[b], %	18.5	8.5	10.5	27.2	8.1	9.7	30.9	10.2	9.1	37.8	8.2	9.5	46.2
Volatile solids, g/l	0.074	0.085	0.105	0.1088	0.081	0.097	0.1236	0.102	0.091	0.1512	0.082	0.095	0.081
Wavelength, nm													
600	0.16	0.09	0.10	0.35	0.04	0.03	0.42	0.11	0.13	0.53	0.15	0.07	0.61
580	0.17	0.11	0.10	0.43	0.05	0.05	0.53	0.11	0.15	0.68	0.15	0.09	0.65
570	0.19	0.11	0.10	0.48	0.05	0.05	0.59	0.14	0.16	0.76	0.15	0.09	0.70
560	0.22	0.13	0.14	0.54	0.06	0.06	0.68	0.16	0.17	0.85	0.17	0.11	0.75
550	0.24	0.15	0.15	0.59	0.07	0.08	0.75	0.18	0.18	0.94	0.19	0.12	0.82
540	0.27	0.16	0.16	0.68	0.09	0.09	0.85	0.18	0.20	1.06	0.21	0.15	0.91
530	0.28	0.16	0.16	0.75	0.09	0.09	0.94	0.20	0.20	1.17	0.22	0.17	1.01
520	0.30	0.18	0.16	0.84	0.09	0.09	1.07	0.22	0.20	1.30	0.23	0.18	1.10
510	0.35	0.20	0.19	0.94	0.14	0.12	1.13	0.25	0.23	1.46	0.27	0.22	1.19
500	0.41	0.20	0.23	1.03	0.15	0.13	1.35	0.30	0.28	1.44	0.32	0.27	1.27
490	0.43	0.23	0.24	1.16	0.16	0.15	1.50	0.34	0.29	1.80	0.35	0.31	1.43
480	0.50	0.25	0.25	1.30	0.16	0.15	1.69	0.37	0.33	2.00	0.41	0.36	1.60
470	0.58	0.28	0.28	1.46	0.17	0.18	1.90	0.41	0.35	2.25	0.45	0.42	1.79
465	0.61	0.29	0.29	1.54	0.20	0.18	2.02	0.43	0.38	2.37	0.49	0.45	1.90
460	0.62	0.29	0.29	1.64	0.22	0.20	2.13	0.46	0.39	2.48	0.50	0.47	2.00
455	0.66	0.31	0.32	1.73	0.23	0.22	2.27	0.49	0.39	2.64	0.53	0.52	2.11
450	0.72	0.34	0.35	1.83	0.25	0.24	2.39	0.50	0.44	2.78	0.55	0.56	2.25
420	1.10	0.53	0.54	2.70	0.45	0.38	3.41	0.75	0.65	3.87	0.79	0.89	3.39
400	1.54	0.85	0.84	3.49	0.66	0.56	4.38	1.05	1.01	4.90	1.08	1.24	4.68
380	2.48	1.86	1.74	4.75	1.32	1.08	5.78	1.66	2.03	6.30	1.73	1.92	6.94

[a] 1/(g)(cm), obtained by dividing absorbance values with volatile solids in g/l.

[b] Based on total solids.

For sample code see Table 1.

Table 7. ABSORPTIVITY[a] VALUES OBTAINED FROM ULTRAVIOLET SPECTRUM AT pH 7.6 OF WASTES FROM IPCO

	100% Decker			25% Decker, 25% Caustic			50% Decker, 50% Caustic			100% Caustic			
	UD8	LTBC8	LTAC8	UDC7	LTBC7	LTAC7	UDC9	LTBC9	LTAC9	UC10	LTBC10	LTAC10	Indulin-C
Total solids, g/l	0.2	0.5	0.5	0.02	0.5	0.5	0.02	0.4	0.5	0.02	0.5	0.5	0.018
Volatile solids[b], %	18.2	8.5	10.5	27.2	8.1	9.7	30.9	10.2	9.1	37.8	8.2	9.5	46.2
Volatile solids, g/l	0.037	0.0425	0.0525	0.0054	0.0405	0.0485	0.0062	0.0408	0.0455	0.0076	0.041	0.0475	0.008
Wavelength, nm													
340	5.57	4.77	4.42	7.04	2.89	2.64	10.17	3.51	4.66	10.26	3.76	4.04	16.6
320	6.98	4.82	4.44	9.44	3.46	3.09	12.26	4.66	6.20	11.97	5.10	5.66	21.6
300	8.65	5.00	4.71	13.15	4.20	3.73	15.50	6.05	8.00	15.26	7.13	7.64	27.6
295	9.49	5.48	5.09	13.89	4.69	4.01	16.62	6.86	8.90	16.32	7.93	8.59	30.6
290	10.05	5.95	5.70	14.99	5.36	4.80	18.23	7.72	10.04	17.63	9.20	9.77	33.5
285	11.92	6.60	6.50	16.66	6.17	5.32	19.68	8.87	11.43	18.82	10.59	11.16	37.0
282	12.47	7.22	6.97	17.41	6.49	5.75	20.33	9.41	12.28	19.47	11.45	11.96	38.0
280	12.70	7.34	7.11	17.59	6.86	5.98	20.81	9.78	12.55	20.00	11.76	12.36	38.4
278	12.89	7.48	7.19	17.77	7.11	6.04	21.14	10.07	12.95	20.13	12.16	12.74	38.8
275	13.19	7.83	7.58	18.33	7.43	6.39	21.78	10.49	13.58	20.76	12.72	13.35	38.8
270	13.49	8.11	7.78	19.44	7.78	6.64	23.07	10.93	14.13	21.98	13.26	14.00	38.6
265	13.67	8.33	7.96	19.63	7.87	6.76	23.56	11.08	14.33	22.52	13.40	14.19	38.4
260	14.22	8.73	8.29	20.00	7.98	6.86	24.04	11.10	14.35	23.03	13.25	14.08	39.0
255	15.13	9.55	8.92	20.18	8.07	7.01	24.36	11.10	14.06	23.55	12.93	13.77	40.9
250	16.43	10.16	9.47	21.66	8.32	7.21	25.49	11.12	14.19	24.35	12.78	13.68	44.6
240	21.38	12.09	11.53	26.48	9.26	8.14	29.36	11.89	15.14	28.16	13.44	14.37	60.5
235	24.46	13.88	13.26	30.37	10.20	9.03	32.42	12.99	16.36	30.79	14.56	15.49	71.1
230	27.00	15.55	15.07	33.33	11.31	10.02	37.92	14.22	17.89	33.82	16.13	17.03	80.3
225	29.90	17.81	17.28	38.38	12.94	11.49	39.52	16.08	20.16	37.37	18.51	19.30	88.9
220	32.38	20.78	19.81	41.67	15.16	13.46	43.39	18.58	22.90	41.19	18.46	22.40	98.6
215	38.69	24.17	23.34	46 66	18.00	15.98	47.60	21.61	26.79	45.00	25.45	26.29	114.1
205	55.14	37.[illegible]6	35.37	58.13	26.42	23.62	54.86	28.06	35.06	48.42	31.50	33.03	161.1
202	--	--	--	--	--	--	--	30.47	37.32	48.69	33.10	35.15	169.0
200	--	--	--	--	--	--	--	32.08	39.94	48.69	34.54	36.69	169.6

[a] 1/(g) (cm), obtained by dividing absorbance values with volatile solids in g/l.

[b] Based on total solids.

For sample code see Table 1.

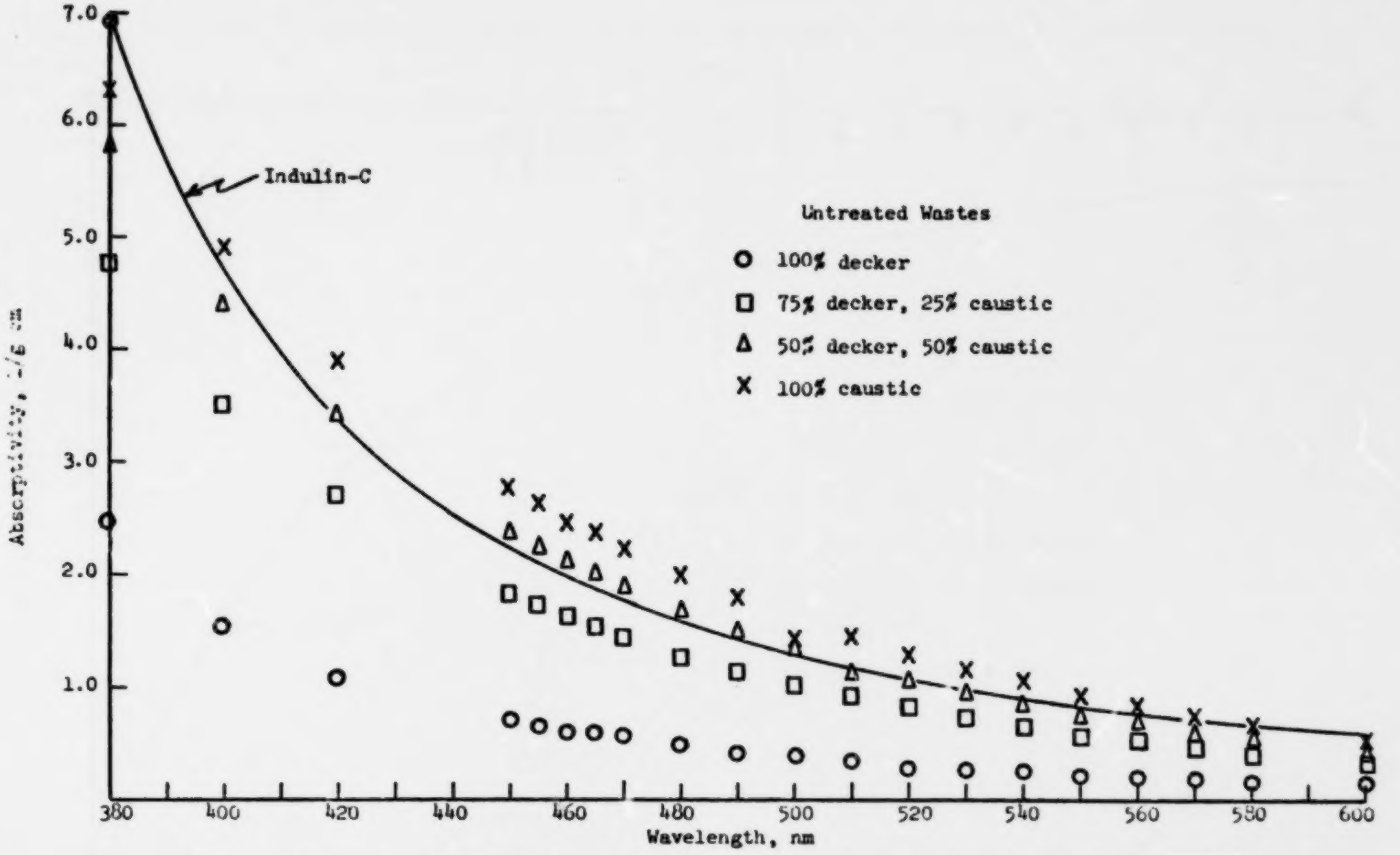

Figure 3. Absorptivity values at pH 7.6 of untreated wastes from IPCO (visible region)

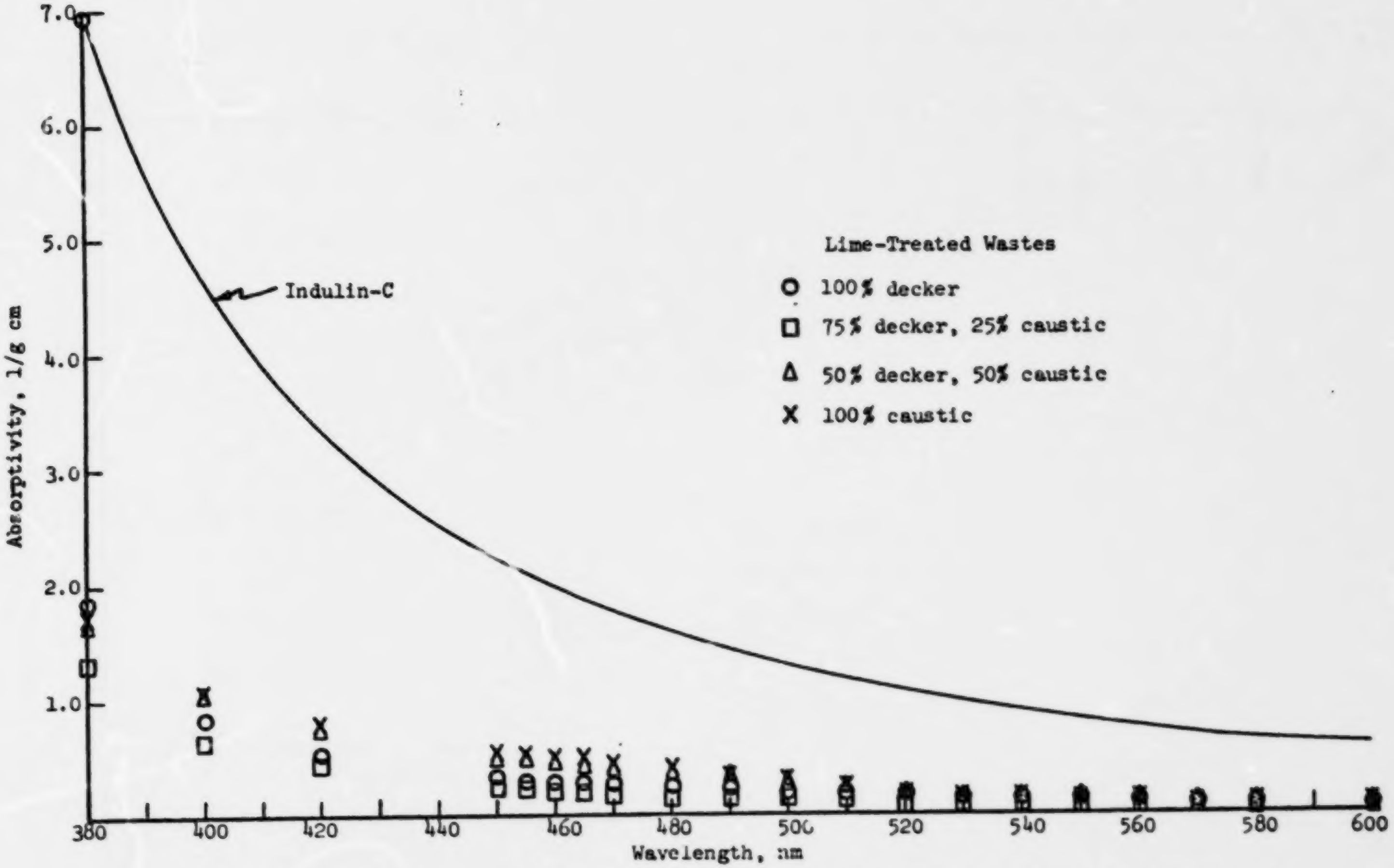

Figure 4. Absorptivity values of pH 7.6 of lime-treated wastes from IPCO (visible region)

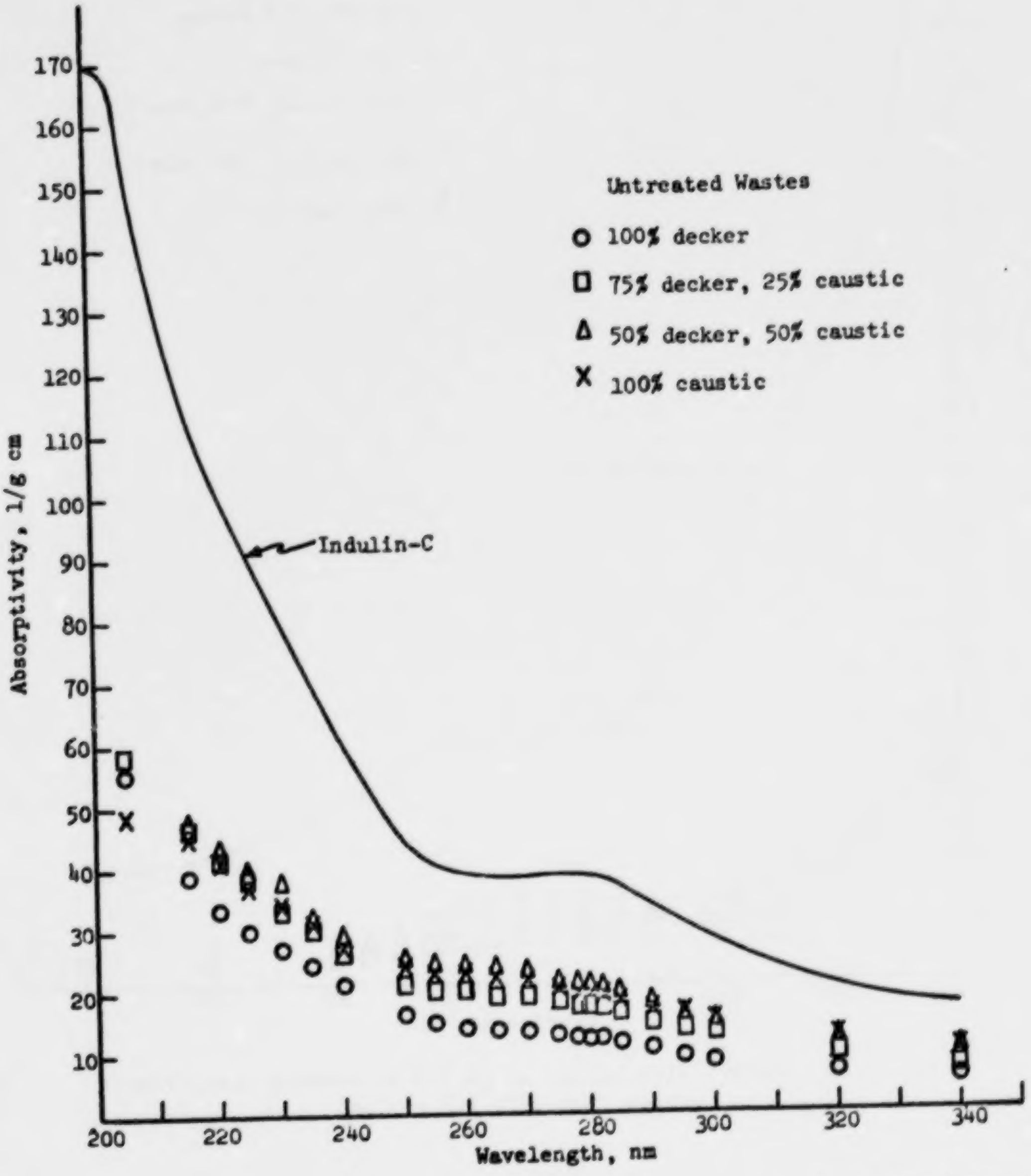

Figure 5. Absorptivity values at pH 7.6 of untreated wastes from IPCO (UV region)

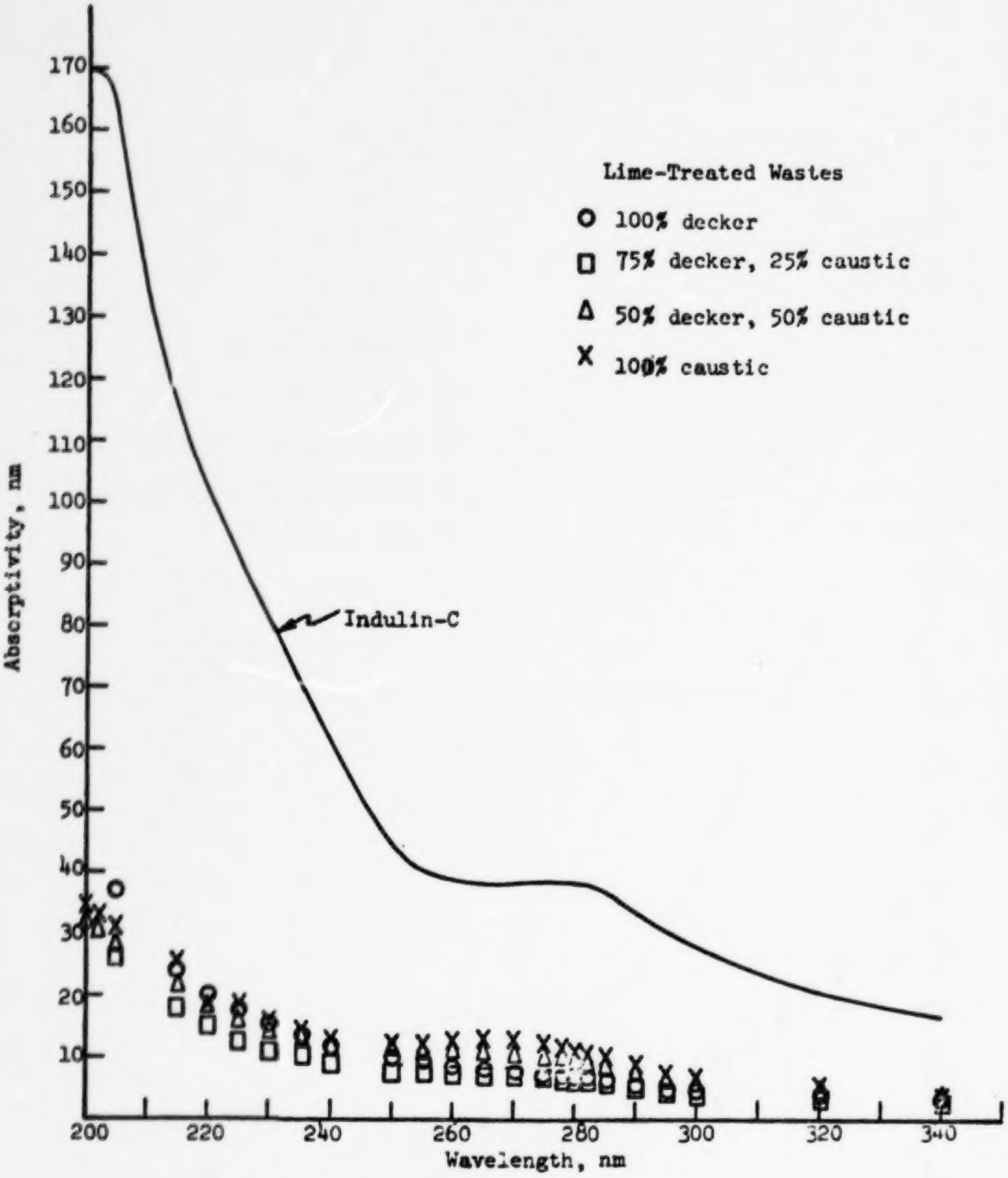

Figure 6. Absorptivity values at pH 7.6 of massive lime-treated wastes from IPCO (UV region)

The following is observed:

Visible Region (Figures 3 and 4) –

a. All samples exhibit increased absoptivity as the wavelength decreases.
b. None of the samples contain a maximum in this region.
c. Untreated samples containing higher percentages of caustic extract give higher absorptivity values, with 100 percent caustic having the highest, even higher than Indulin-C (Figure 3).
d. Lime-treated samples exhibit similar but lower absorptivities than their respective untreated samples (Figure 4).

The visible spectra demonstrated that no single color is present in the waste samples, rather they are mixtures of different colors as characterized by the increase in absorptivity as the wavelength decreases. In addition, it was demonstrated that lime treatment decreases the amount of color-giving materials.

Ultraviolet Region (Figures 5 and 6) –

a. The samples exhibit increased absorptivities as the wavelength decreases.
b. Untreated samples from the decker stage have lowest absorptivity values compared to others (Figure 5).
c. Lime-treated samples exhibit similar but lower absorptivities than their respective untreated samples (Figure 6).
d. All samples show a "shoulder" at about 280 nm. A similar "shoulder" was noticed at 205 nm in some cases. These absorptivity curves are quite similar to the one exhibited by Indulin-C.
e. Generally, samples containing higher percentages of untreated caustic extract gave higher absorptivity values with a shift in the absorptivity "shoulder" from 280 nm to 265 nm. The reason for this shift is not understood. Chlorinated lignins may have something to do with this. Hardwood lignins are

known to have maxima (shoulder) at shorter wavelengths than softwood lignins, about 275 instead of 280 nm[12]. Goring[13] has cited 272 nm as the position for the maximum for birch lignin.

The ultraviolet spectra indicated that the mill wastes contain materials similar to those present in lignin and that the amount of these materials is decreased by lime treatment.

Effect of Lime Treatment

The percentage of color and TOC removal and percentage decrease in absorptivity were calculated from data in Tables 1, 6, and 7 and the results are given in Table 8 and plotted in Figures 7 and 8.

Table 8. EFFECT OF LIME TREATMENT ON WASTES FROM IPCO

Composition of mill effluent				Decrease in absorptivity[b], %	
Caustic, %	Decker, %	Color removal[a], %	TOC removal[a], %	at 420 nm	at 280 nm
0	100	73.0	53.0	54.6	42.2
25	75	95.8	69.4	83.3	61.0
50	50	93.3	79.4	78.0	53.0
100	0	96.2	80.3	79.6	42.5

[a] Based on values for effluent samples.
[b] Decrease in absorptivity caused by lime treatment based on volatile solids content of solids isolated from effluents.

The data show that 74 to 96 percent of color and 53 to 80 percent of TOC are removed during lime treatment. The effectiveness of lime generally increases with increasing amounts of caustic extract in mill effluent (Figure 7). The decrease in absorptivity ranged from 54 to 83 percent at 420 nm and 42-61 percent at 280 nm (Figure 8).

In order to understand the changes due to lime treatment and to avoid the problems of mixed systems, only decker and caustic extract effluents as such were used for further study. Mixed effluents containing 50-50 or 75-25 percent decker and caustic effluents were not investigated in detail.

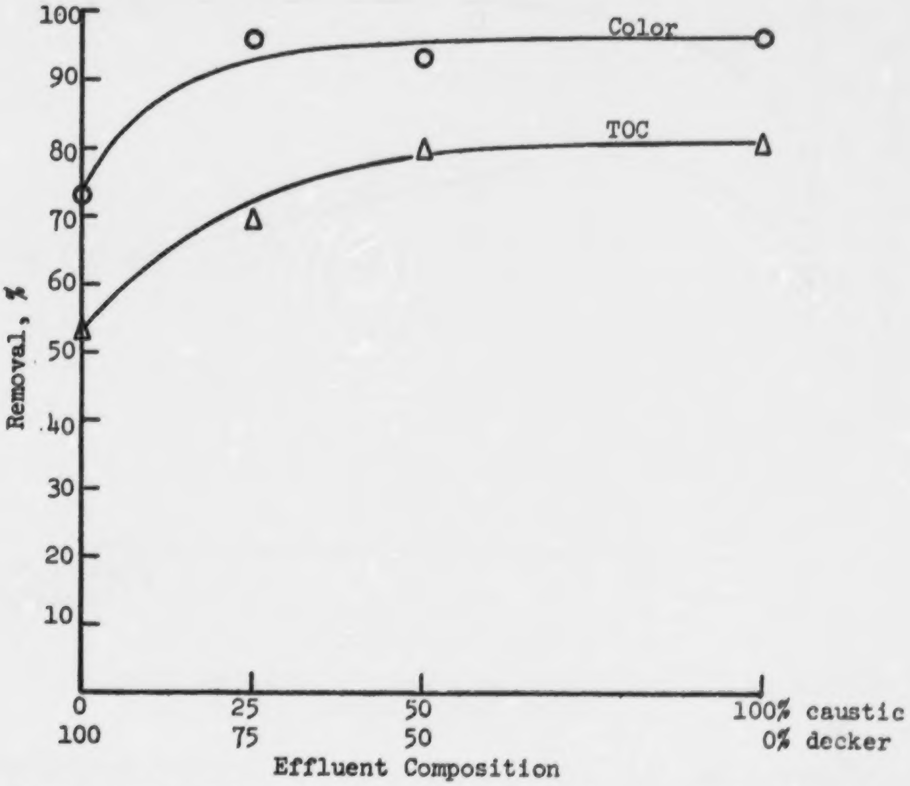

Figure 7. Color and total organic carbon removal of wastes from IPCO by lime treatment

FURTHER CHARACTERIZATION OF COLOR BODIES FROM KRAFT DECKER EFFLUENT FROM IPCO

Fractionation of Color Bodies

Acidification –

From previous experience[9] it was known that most of the colored material could be precipitated by acidification of the strong aqueous solutions of the color bodies from kraft decker wastes. Thus, when 15 percent solutions of the freeze-dried untreated and lime-treated decker wastes were adjusted to a pH of 1.0 with approximately 3N hydrochloric acid,

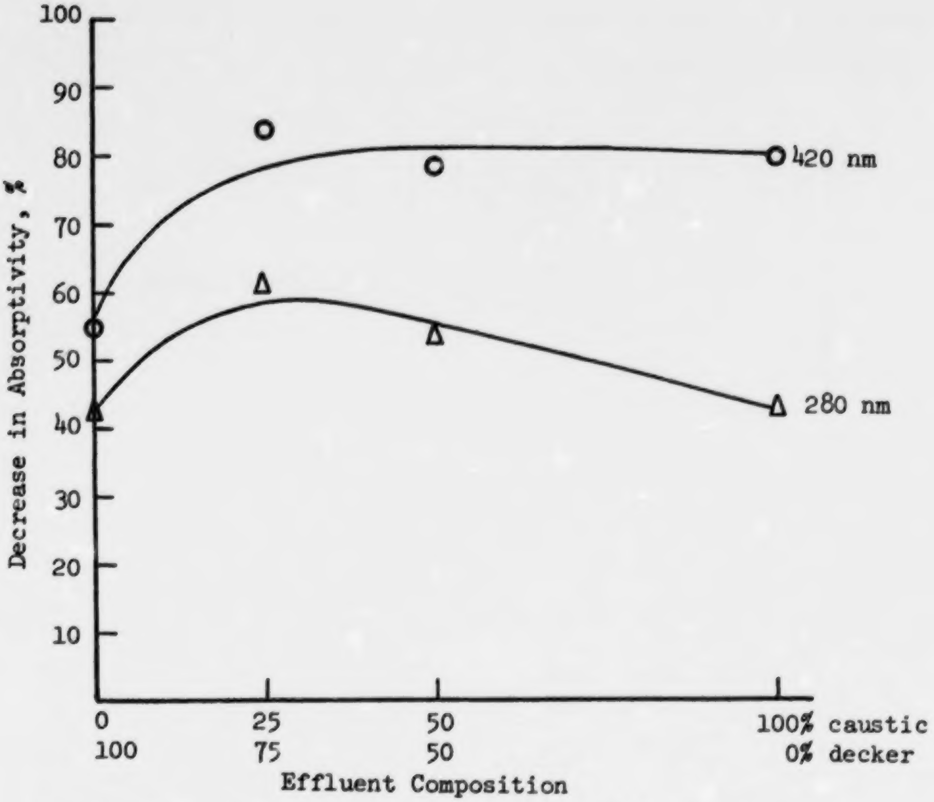

Figure 8. Decrease in absorptivity of wastes from IPCO by lime treatment

much gaseous material was evolved, and a dark colored precipitate was obtained. During acidification an odor similar to that of hydrogen sulfide was also detected. However, the major part of gases is believed to be due to the presence of carbonates in the parent sample. Thus, acidification was used to isolate the acid-insoluble and acid-soluble color bodies. The results of this fractionation are given in Table 9.

The data in Table 9 show that upon acidification of untreated wastes, 82.5 percent color and 51.0 percent TOC were recovered in the acid-insoluble fraction. The acid-soluble fraction contained 17.5 percent color and 49.0 percent of the TOC. However, when lime treated wastes were acidified, the acid-insoluble fraction contained only 51.0 percent color (13.8 out of 27.0) and 7.0 percent TOC (3.3 out of 47.0). The acid-soluble fraction of the lime treated waste contained 49.0 percent color (13.2 out of 27.0) and 93.0 percent TOC (43.7 out of 47.0). Table 9 further shows that the lime treatment removed 83.3 percent color and 93.5 percent TOC from the acid-insoluble color bodies and only 24.5 percent color and 10.8 percent TOC from the acid-soluble color bodies. These values were calculated from the yield data of the untreated and lime-treated color bodies.

Table 9. CHANGE IN SOLIDS ISOLATED FROM IPCO EFFLUENTS DUE TO MASSIVE LIME TREATMENT

	Untreated decker waste		Lime-treated decker waste		Reduction due to lime[c]	
Fractions	Color[a] yield, %	TOC[b] yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
Decker waste	100	100	27.0	47.0	73.0	53.0
Acid-insoluble	82.5	51.0	13.8	3.3	83.3	93.5
Acid-soluble	17.5	49.0	13.2	43.7	24.5	10.8

Yield values basis untreated decker solids.

[a] APHA units, Pt-Co color.
[b] Total organic carbon.

Column Chromatography —

The acid-insoluble color bodies were dissolved in distilled water and fractionated on Bio Gel P-2 column (200-cm long and 2.5 cm in diameter) having an exclusion limit of molecular weight 2600. The first fraction "A" from each run was further fractionated on Bio Gel P-60 column (100 cm long, 2.5 cm diameter) having an exclusion limit of molecular weight 60,000. The details of fractionation are given in the experimental part of this report. All fractions obtained from the gel columns were analyzed for color, TOC, and absorbance at 420 nm and 280 nm. The data were used for calculating percentages of yield and percentage of removal by lime in each fraction. Only data on color and TOC are given in Table 10. (For details see Appendix I.)

Table 10. FRACTIONATION OF DECKER ACID-INSOLUBLE COLOR BODIES BY COLUMN CHROMATOGRAPHY

Fractions	Untreated acid-insoluble color bodies		Lime-treated acid-insoluble color bodies		Reduction due to lime[c]	
	Color yield, %	TOC yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
Fraction "A" from P-2 through P-60 column						
A_1	12.9	6.2	3.6	0.41	72.1	93.4
A_2 through A_6[a]	42.1	15.7	1.0	0.11	97.6	99.3
Acid-insoluble color bodies through P-2 column						
A	55.0	21.9	4.6	0.52	91.6	97.6
B	2.4	1.7	1.0	0.18	58.3	89.4
C	2.1	2.1	1.1	0.24	47.5	88.6
D through R[b]	23.0	25.3	6.1	2.4	73.5	90.5
Unfractionated acid-insoluble color bodies	82.5	51.0	13.8	3.3	83.3	93.5

Percentages of yield are calculated on the basis of untreated original waste.

[a] Calculated by difference so that values for A = (A_1 + A_2 through A_6).

[b] Calculated by difference so that values for unfractionated acid-insoluble color bodies = (A + B + C + D through R).

[c] Values calculated from "yield" data of the solids isolated from untreated and lime-treated effluents.

The results show that in the case of untreated acid-insolubles approximately 67 percent of the color (55.0 out of 82.5) and 43 percent TOC (21.9 out of 51.0) were obtained in fraction "A," whereas in the case of lime-treated acid-insolubles this fraction contained only 33 percent of the color and 15.7 percent of TOC. Average color and TOC removed by lime were 83.3 and 93.5 percent, respectively.

The untreated and lime-treated acid-soluble color bodies were isolated into four fractions by first sorbing on Rohm & Haas Company's Amberlite

XAD-8 resin (polystyrene cross-linked with divinyl benzene) and then desorbing with aqueous ethanol (1:1 mixture of water and 95 percent ethanol). It should be kept in mind that the fractionation was not sharp, and thus each fraction could contain some material similar to that found in the previous fraction. The ethanol was removed under reduced pressure and each fraction was made alkaline with sodium hydroxide to pH about 9.0.

The first fraction contained material which passed unadsorbed through the column.

The second fraction contained material which was held on the column initially, but was readily eluted from the column with water. Upon alkalization this fraction deepened in color and was more highly colored than the first fraction.

The third fraction was an intermediate fraction and was collected until the eluate was neutral to Congo red.

The fourth fraction contained material eluted with aqueous ethanol.

All fractions obtained from the XAD-8 column were analyzed as before and the results are given in Table 11. The results show that in that case of untreated acid-solubles approximately 62 percent color (10.9 out of 17.5) and 33 percent TOC (16 out of 49.0) were obtained in fraction IV. (Some color and TOC is unaccounted for), whereas in the case of lime-treated acid-solubles this fraction contained 70 percent color and 30 percent TOC. The average color and TOC removed by lime were 24.5 and 10.8 percent, respectively. The table further shows that practically no color and TOC are removed by lime from acid-soluble Fractions III and IV (when calculated on the combined basis).

Characterization of Decker Effluent Fractions

Fractions of acid-insoluble and acid-soluble color bodies of the untreated wastes were obtained by column chromatography. Several of these fractions were very small, especially after allowing for amounts required for molecular weight determinations.

Table 11. FRACTIONATION OF DECKER ACID-SOLUBLE COLOR BODIES BY SORPTION ON XAD-8 RESIN

Fractions	Untreated acid-soluble color bodies		Lime-treated acid-soluble color bodies		Reduction due to lime[a]	
	Color yield, %	TOC yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
(Combined III + IV)	(12.1)	(19.0)	(12.0)	(20.1)	(1.0)	(+5.0)
IV	10.9	16.0	9.2	12.9	15.5	19.5
III	1.2	3.0	2.8	7.2	+	+
II	2.5	16.2	1.3	14.7	48.0	9.2
I	0.9	7.6	0.5	4.9	44.5	35.5
Unfractionated acid-soluble color bodies	17.5	49.0	13.2	43.7	24.5	10.8

Percentages of yield are calculated on the basis of untreated organic waste. "+" Values showed an increase.

[a] Values calculated from "yield" data of the solids isolated from untreated and lime-treated effluents.

To provide sufficient material for chemical analysis some adjacent fractions were combined to give bulky fractions. Thus, Fractions "A_1" through "A_6" were combined (referred to as "A"), "C" through "R" were combined, and out of the four acid-soluble fractions the adjacent fractions which were similar with respect to their ratios of color to organic carbon were combined to give two larger fractions.

Visible and Ultraviolet Spectra —

Visible and ultraviolet spectra of Indulin-C, acid-insoluble fractions, and acid-soluble fractions of the untreated and lime-treated wastes were determined at pH 7.6.

Absorptivity values from these spectra were calculated at definite wavelengths and the results are plotted in Figures 9, 10, 11, and 12.

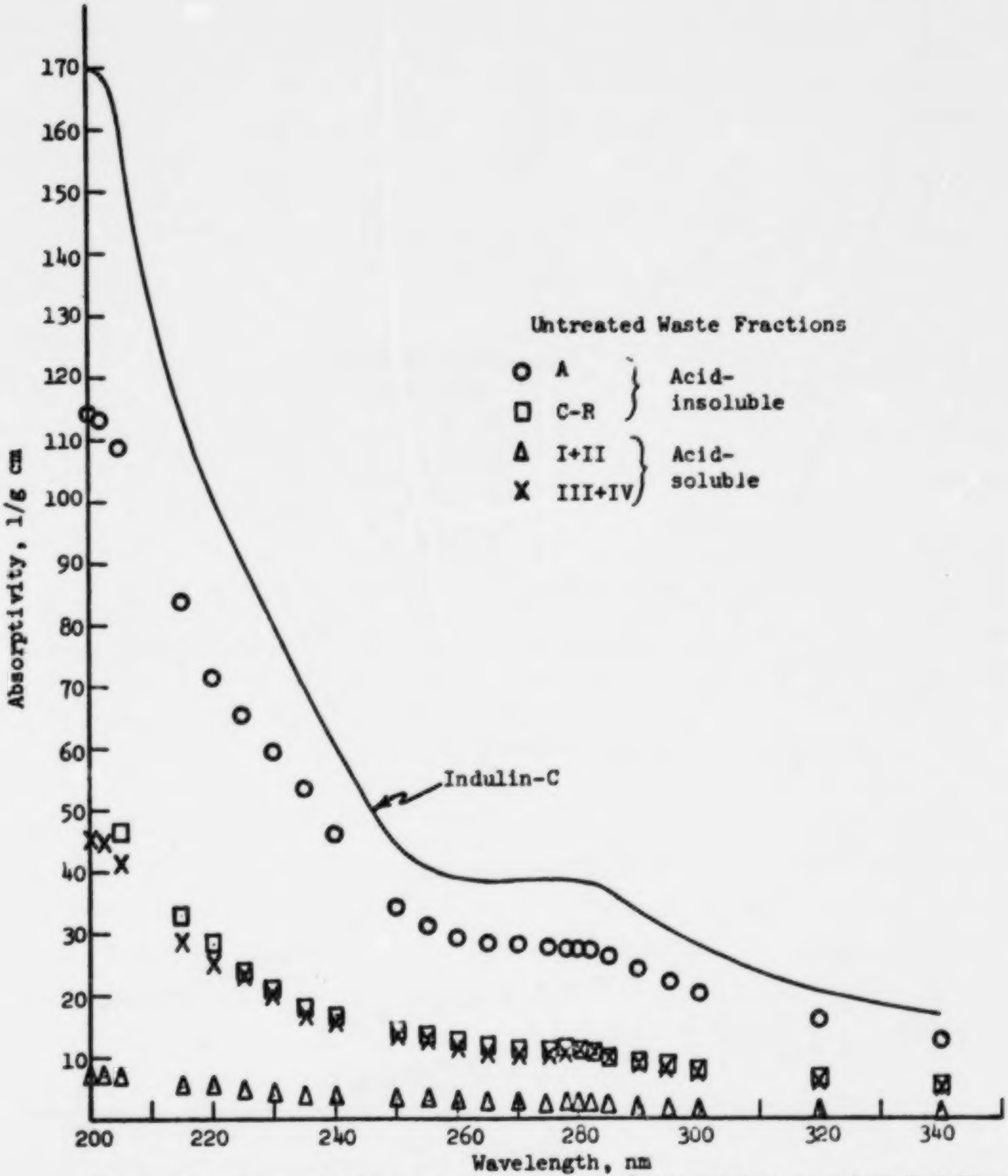

Figure 9. Absorptivity versus wavelength (ultraviolet range) of Indulin-C and untreated kraft decker waste from IPCO

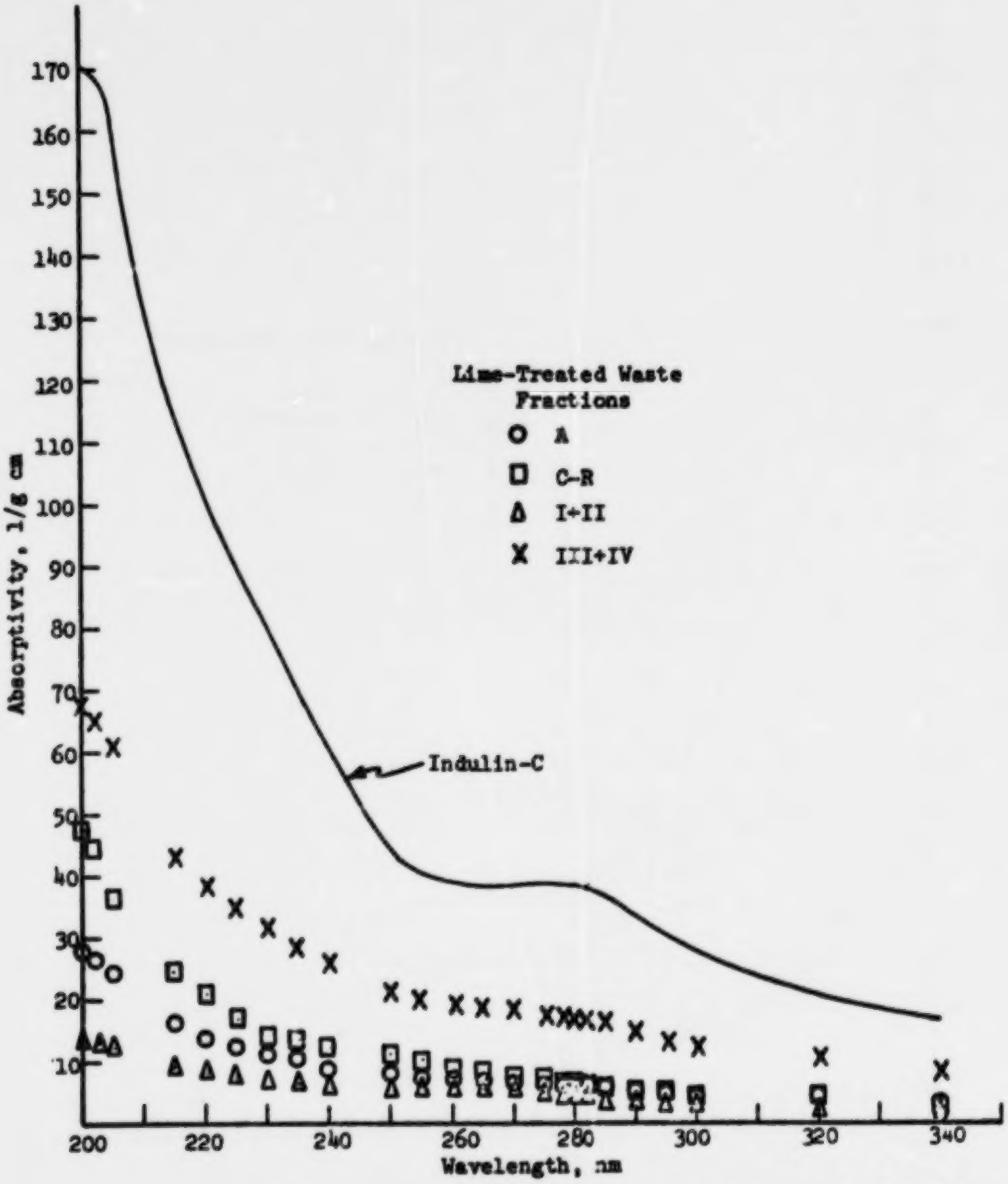

Figure 10. Absorptivity versus wavelength (ultraviolet range) of Indulin-C and lime-treated kraft decker waste from IPCO

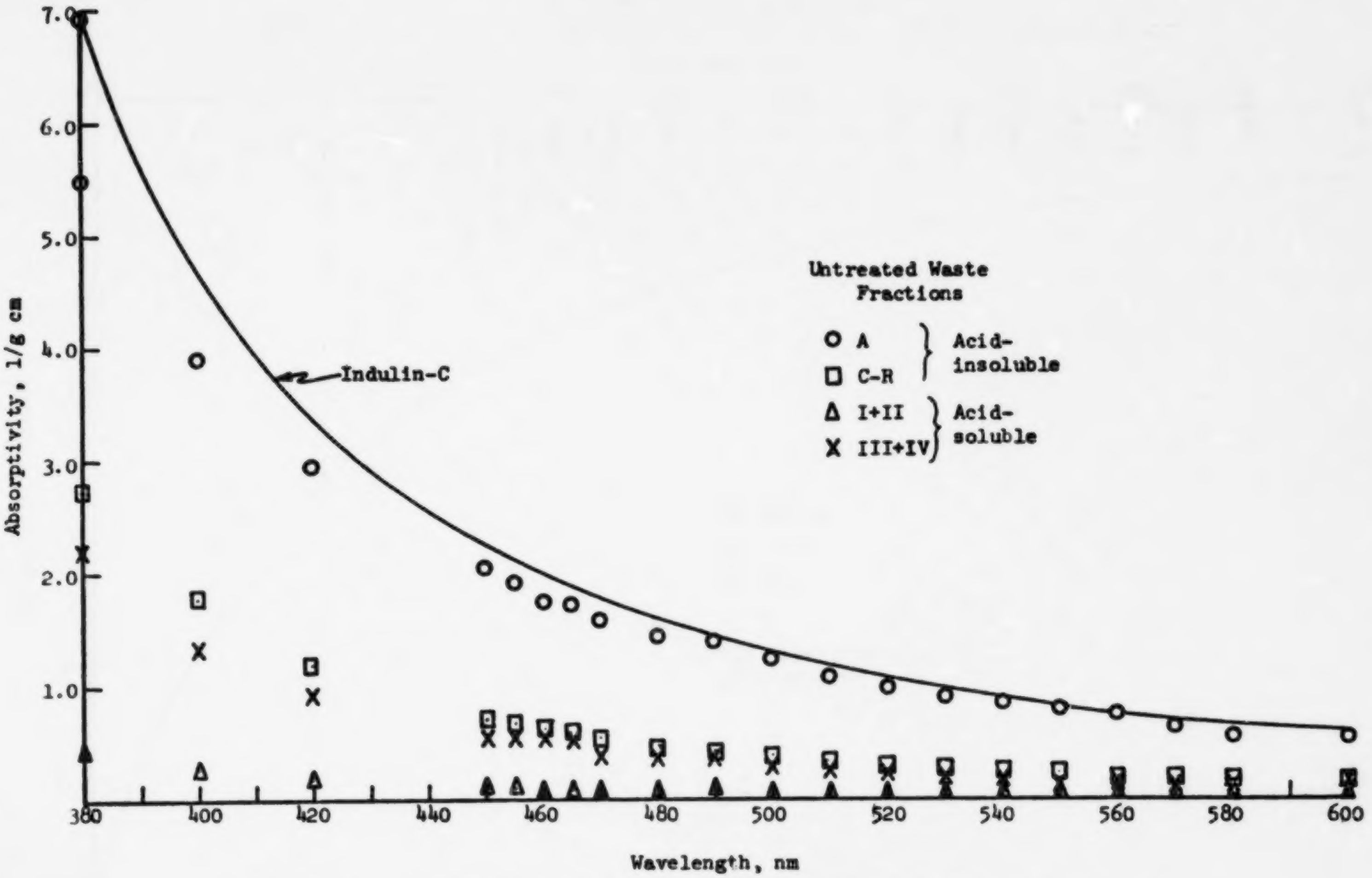

Figure 11. Absorptivity versus wavelength (visible range) of Indulin-C and untreated kraft decker waste from IPCO

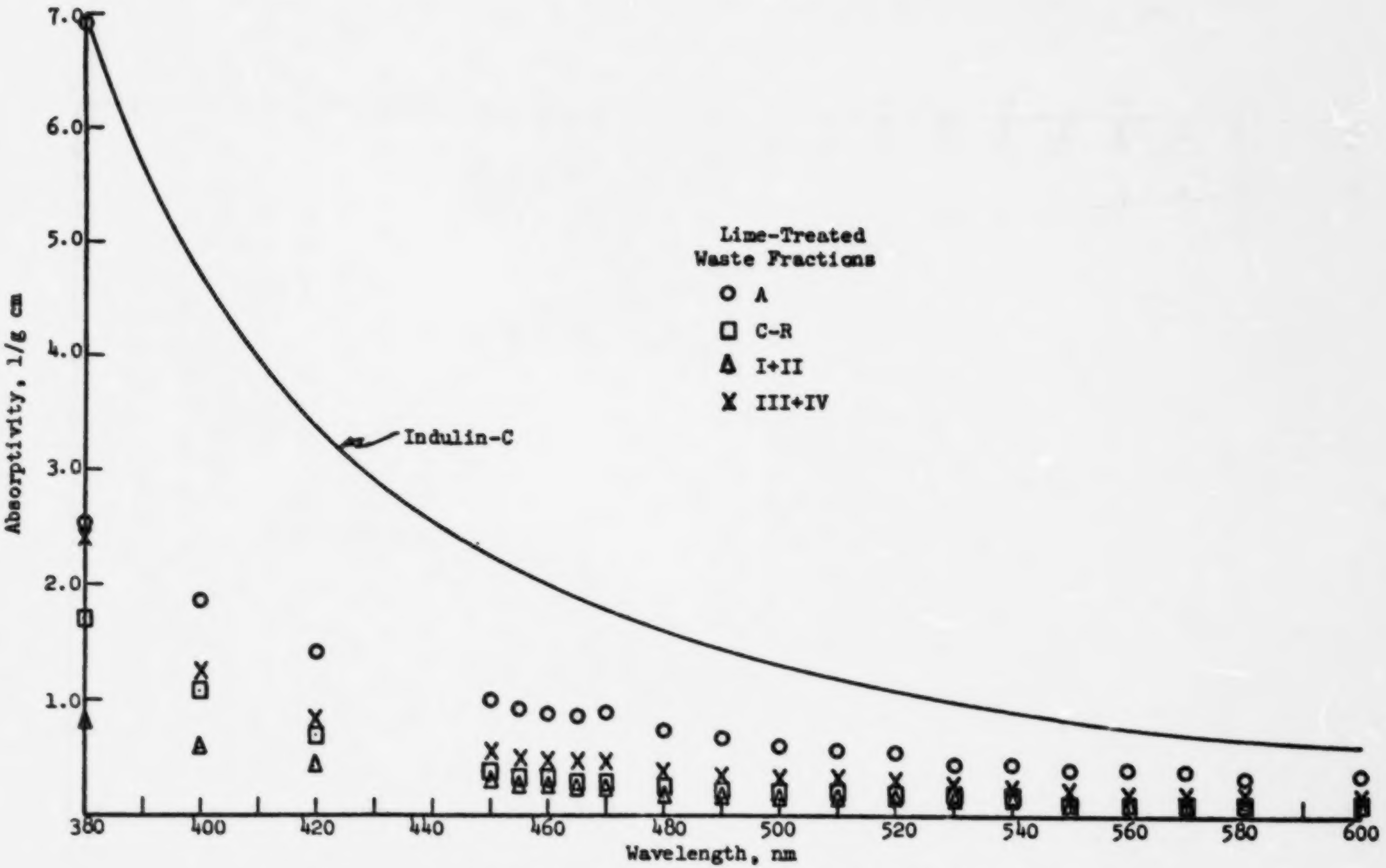

Figure 12. Absorptivity versus wavelength (visible region) of Indulin-C and lime-treated kraft decker waste

Ultraviolet region (Figures 9 and 10) — All samples exhibited an increase in absorptivity as the wavelength decreased. Indulin-C, untreated "A" fraction, untreated III and IV fraction and lime-treated III and IV fractions showed an Indulinlike characteristic absorption band at 280 nm indicating the presence of more ligninlike materials. The lime-treated color bodies of the acid-insolubles (Fractions "A" and C-R) showed lower absorptivity values than their respective untreated fractions. However, the acid-soluble color bodies (Fractions I + II and III + IV) showed an increase in absorptivity after lime-treatment (compare Figures 9 and 10).

Visible region (Figures 11 and 12) — All samples gave simple absorption curves and exhibited an increase in absorptivity as the wavelength decreased.

Acid-insoluble color bodies (Fractions A and C-R) showed lower absorptivities after lime-treatment while the absorptivities of acid-soluble color bodies (Fractions I + II and III + IV) increased or remained unchanged after lime treatment.

At this stage it can be said that almost all fractions contain ligninlike color bodies. The differences in absorptivity may be due to different levels of degradation of color bodies.

Molecular Weight Distribution —

Molecular weights of some selected fractions of acid-insoluble and all acid-soluble components of the untreated and lime-treated color bodies were determined by the sedimentation equilibrium method using the analytical ultracentrifuge[14]. In the present work the "short column sedimentation equilibrium method" was used. Details of this method are given in the Experimental part. The apparent "Weight Average" molecular weights (M_w) for each fraction were calculated at zero angular velocity ($\omega^2 = 0$) because the M_w were changing with change in ω^2. The results are plotted in Figures 13a and b.

Figure 13a shows that untreated acid-insoluble components are much higher in M_w than those of lime-treated acid-insolubles. The M_w values drop

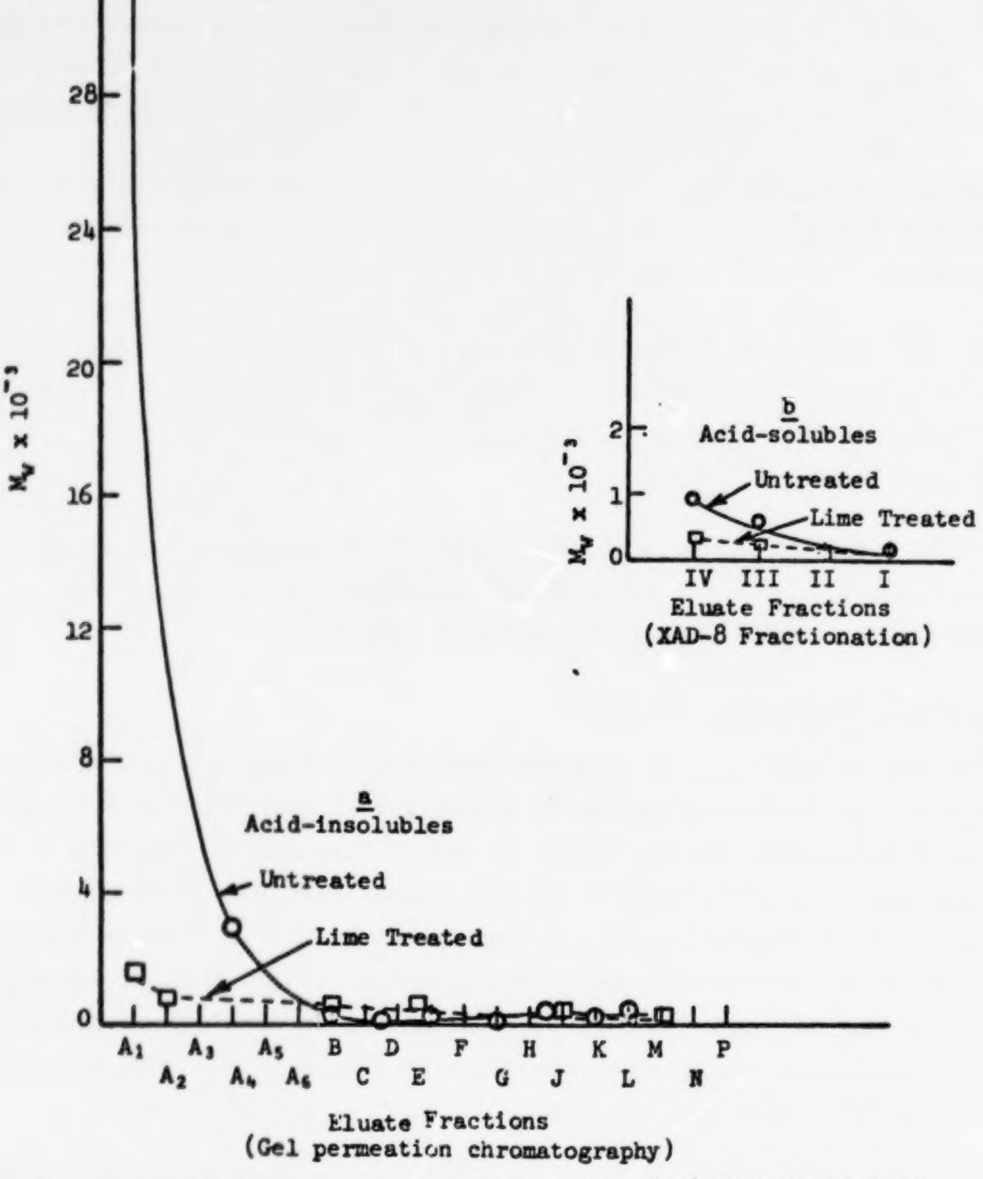

Figure 13. Weight average molecular weight (M_w) distribution of fractionated color bodies from kraft decker effluent from IPCO (M_w values at $\omega^2=0$)

sharply from 33,000 to about 300 and then rise slightly near Fraction "J." The increase, however, is not very significant and may be due to different ash contents of the fractions. The noticeable point of interest is that most of the higher M_w material has been removed by lime.

M_w of untreated and lime-treated acid-soluble color bodies are quite similar to each other (Figure 13b). Lime-treated materials (M_w range < 350) have, however, lower M_w than untreated materials (range < 950).

Figure 14 shows that acid-insoluble color bodies having an apparent M_w of less than 200 are not removed by the massive lime treatment. The intermediate range of M_w 200 to 2000 apparently undergoes partial removal and over 2000 are completely removed. However, over 80 percent removal occurs above a M_w of 200-500. The average color and TOC removal of the acid-insoluble fraction was found to be 83.3 and 93.5 percent, respectively (Table 10).

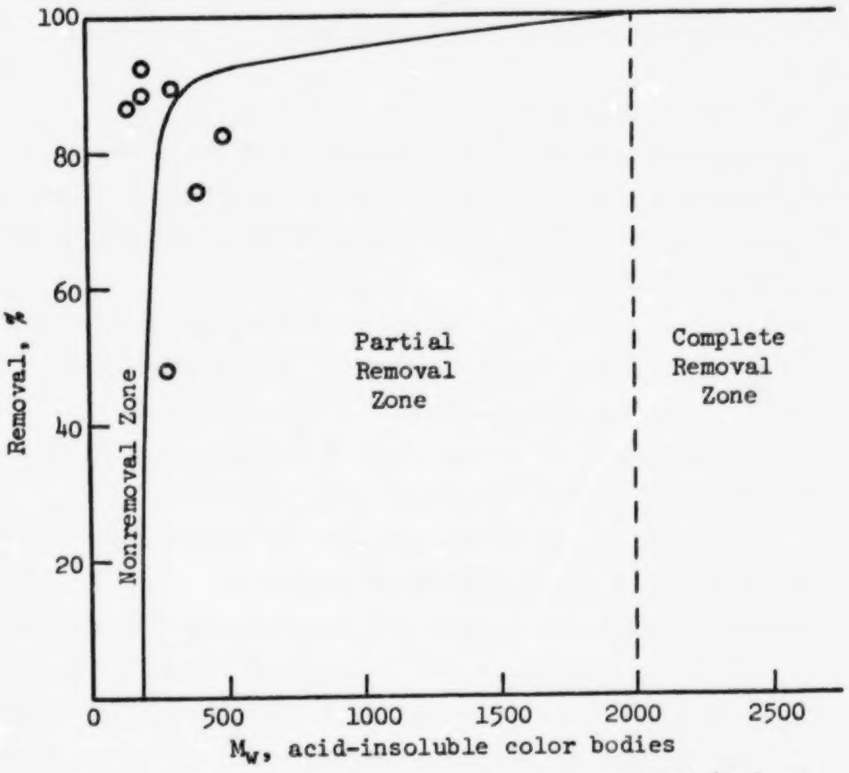

Figure 14. Weight average molecular weight (M_w) of acid-insoluble color bodies from decker effluent versus percentage of removal by massive lime

The acid soluble color bodies behave differently. In this case color bodies which were sorbed on XAD-8 resin and later desorbed by aqueous ethanol (Fractions III + IV) were practically untouched by lime, while 21 percent removal occurred in the case of color bodies which could not be sorbed on XAD-8 resin. The average color and TOC removal of the acid-soluble fractions was only 24.5 and 10.8 percent, respectively.

Chemical Characterization –

The results of the chemical analysis are given in Table 12. Fractions were analyzed for ash, phenolic hydroxyl, total sugars, and methoxyl content. Absorptivities (absorbance/volatile solids in g/liter) at 420 nm (E_{420}), as a measure of original color, and at 280 nm (E_{280}) as a measure of lignin content have also been tabulated. Actually two values may be used as approximate measure of lignin content, namely E_{280} and methoxyl. Calculated ratios of E_{420}/E_{280}, E_{465}/E_{600}, E_{420}/MeO, and E_{280}/MeO have also been included in Table 12.

The data in Table 12 suggest:

a. The untreated decker waste contains 0.25 meq phenolic hydroxyl per gram of volatile solids, whereas the lime-treated waste contains 0.07 meq/g volatile solids, about 73 percent reduction.

b. Total sugar content is reduced from 16.41 g/100 g volatile solids to 6.0 g by lime-treatment. A reduction of 63.4 percent. (For individual sugars see Appendix II.)

c. Methoxyl content of decker waste is reduced from 6.44 to 3.18 percent by lime treatment (50.5 percent). Acid-soluble fractions "I + II" contain the lowest amount of MeO indicating least ligninlike character.

d. Ratios, E_{420}/MeO, E_{280}/MeO, and E_{420}/E_{280} indicate that except for some greater loss in methoxyl, lignins in the untreated waste are very similar to the lignins in Indulin-C. The lignins in the lime-treated waste appear to be more degraded.

Table 12. ANALYTICAL DATA ON FRACTIONS OF DECKER EFFLUENT FROM IPCO
(Basis o.d. volatile solids)

	Indulin-C	Untreated decker					Lime-treated decker				
		Original	Acid-insoluble		Acid-soluble		Original	Acid-insoluble		Acid-soluble	
			A	C-R	III+IV	I+II		A	C-R	III+IV	I+II
Mol. wt. range	--	100-33,000	3,000-33,000	170-500	600-930	100-150	150-1,300	800-1,800	150-680	250-330	<170
Color recovery, %	--	--	66.7	30.4	69.2	19.4	--	33.4	52.2	91.0	13.6
Ash[a], %	53.80[c]	81.5	38.54	63.86	31.58	90.94	91.5	ND	70.75	38.89	79.24
Volatile solids[b], %	46.20	18.5	61.46	36.14	68.42	9.06	8.5	--	29.25	61.11	20.76
Phenolic hydroxyl, meq/g	1.32	0.25	--	--	--	--	0.07	--	--	--	--
Total sugars[d], %	--	16.41	--	--	--	--	6.00	--	--	--	--
Methoxyl (MeO), %	21.05	6.44	13.54	4.40	4.84	0.89	3.18	ND	3.42	4.87	0.58
E_{420}	3.39	1.10	2.95	1.20	0.92	0.21	0.53	1.43	0.70	0.85	0.44
E_{280}	38.4	13.05	27.74	10.79	10.86	2.53	7.86	6.63	7.00	17.15	4.19
E_{420}/MeO ratio	0.16	0.17	0.22	0.27	0.19	0.24	0.17	--	0.20	0.17	0.76
E_{280}/MeO ratio	1.82	2.03	2.04	2.05	2.24	2.84	2.47	--	2.05	3.52	7.22
E_{420}/E_{280} ratio	0.088	0.084	0.108	0.111	0.085	0.083	0.067	0.216	0.100	0.050	0.105
E_{465}/E_{600} ratio	3.14	3.76	3.18	3.11	3.00	3.64	3.13	2.44	3.54	3.09	3.36

[a] Ashed at 600°C for 1 hour. Ash calculated on o.d. material.
[b] Volatile solids = 100 minus % ash.
[c] Indulin ash values higher than expected.
[d] For individual sugars see Appendex II.

E_{280}, E_{420}, E_{465}, E_{600} are absorptivities at 280, 420, 465 and 600 nm wavelengths.

e. Ratios of E_{465}/E_{600} were calculated on the basis of observations by Ortiz De Serra et al.[15]. The authors have used ratios of E_{465}/E_{665} as an indication of condensed (lower ratios) or open (higher ratios) structures of humic (acid-insoluble) and fulvic (acid-soluble) acids. Our use of E_{600} was mainly due to the reason that E_{665} values were not available and also that over 580 nm not much change in absorptivity was noticed (see Figures 11 and 12). The data suggest that except lime-treated acid-insoluble fraction "A," all other color bodies had structures either similar to or more open than Indulin-C.

Infrared Spectra —

The effect of lime treatment on the organic material is difficult to discern. A new band appears at 1722 in the lime-treated sample, but spectra of the fractions from the original lime-treated sample do not contain such a band nor even a distinct shoulder. Fractionation concentrates the lignin-related systems primarily into untreated acid-insoluble "A" fraction (and its lime-treated analog). In this fraction lignin bands are very prominent compared with carboxylate bands. There is also lignin-related material in the acid-soluble fraction of lower ash content, but the carboxylate absorption is much more intense than the absorption of the aromatic units.

Comparison of the spectra of untreated and lime-treated acid-insoluble fractions "A" suggested that the lime-treated fraction has a significantly higher ratio of carboxylate groups to lignin systems.

(Lime-treated Fraction C-R may be largely composed of an artifact since the spectrum contains many unusual features.)

The IR-spectra were run on samples with ash, whereas references are made to chemical analysis calculated on ash-free basis.

Untreated decker (Figure 15) — This original sample (decker effluent) has very prominent bands at 625 and 1140 cm^{-1}, indicating that appreciable sulfate is present. The presence of carbonate is also suggested

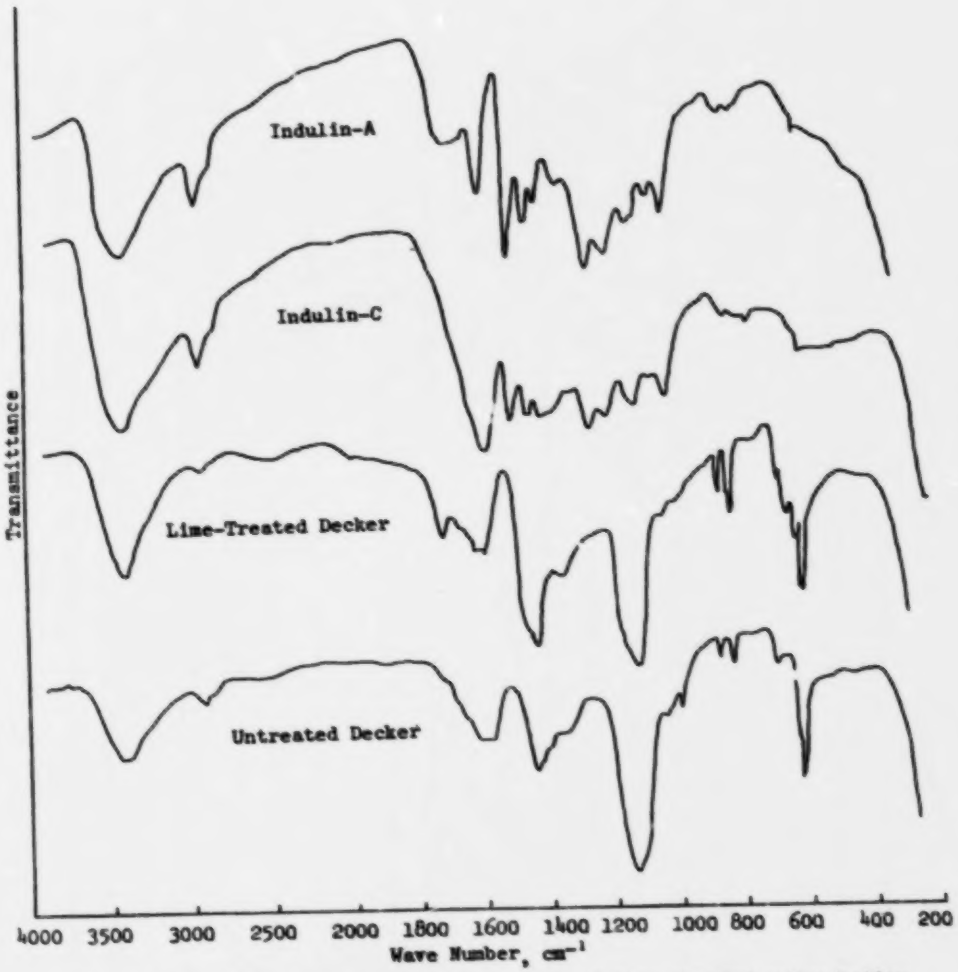

Figure 15. Infrared spectra of untreated and lime-treated color bodies from kraft decker effluent from IPCO, Indulin-C (salt form) and Indulin-A (acid form)

by absorption bands at 1440 and 875 cm^{-1}. The bands at 1600 and the shoulder near 1400 are consistent with bands expected for carboxylate salts.

Lignin-related aromatic systems are undoubtedly present to a small extent. This view is supported by methoxyl analysis (6.44 percent) and a weak band at 1045. A shoulder at 1505 provides further support for lignin. The carboxylate and carbonate bands in this region (1400-1650 cm^{-1}) are far more dominant than the aromatic-related band at 1505.

Lime-treated decker (Figure 15) — The lime-treated sample spectrum, although similar in general appearance to untreated, differs in several ways: 1) the OH/CH ratio is higher (judging from absorbances at 3400 and 2920), 2) a new band is evident at 1722, 3) more intense bands are present at 1440 and 875 probably signifying higher carbonate content, and 4) a new band is seen at 670 cm^{-1}.

Higher inorganic content is supported by a higher ash content and lower methoxyl content (3.18 percent) for the lime-treated sample.

The new band at 1722 may be the result of oxidation occurring during lime-treatment creating carbonyl groups. The interpretation of this band and its significance is uncertain since the band does not appear in any of the subsequent lime-treated fractions.

Untreated acid-insoluble Fraction "A" (Figure 16) — The main differences resulting from the separation of the acid-soluble material are that the sulfate and carbonate contents are markedly reduced and the lignin bands are much more evident. The strong bands at 1582 and about 1400 probably reflect carboxylate salts. Prominent bands at 1505 and 1460 are evidently due to lignin (aromatic skeletal vibrations), and this agrees nicely with the high methoxyl content (13.54 percent). A band at 1030 is also apparent, which is thought to arise in part from in-plane aromatic C-H bonding in lignin. In fact, the bands at 1030, 1135, 1215, and 1264 are probably all lignin-related.

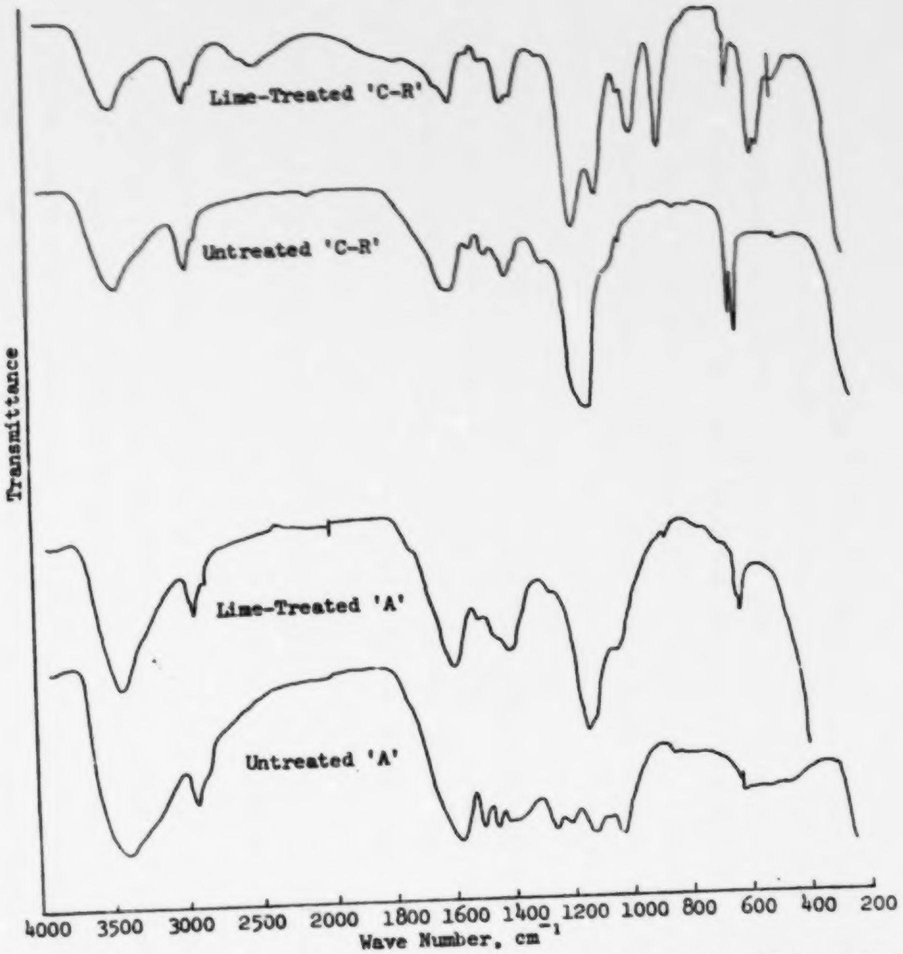

Figure 16. Infrared spectra of untreated and lime-treated acid-insoluble color bodies from kraft decker effluent from IPCO

Lime-treated acid-insoluble Fraction "A" (Figure 16) — The lime-treated decker waste yielded this acid-insoluble fraction which has an IR somewhat similar to that of the untreated Fraction "A." However, this sample seems to have much more sulfate and considerably less lignin. Carboxylate salt is again apparent (1590 and 1440 cm^{-1}) and a weak band at 1505 is probably due to lignin. Comparison of relative intensities of the 1590 band with the band at 1505 suggests that the ratio of carboxylate to aromatic rings is higher in the lime-treated than in the untreated acid-insoluble "A"-fraction.

Untreated acid-insoluble Fractions "C-R" (Figure 16) — This fraction contains substantial sulfate in contrast to the higher molecular weight acid-insoluble Fraction "A." The ash content is markedly higher (64 percent vs. 39 percent), and the methoxyl content is lower (4.4 percent vs. 13.54 percent). The ratio of carboxylate to aromatic rings is appreciably higher in this sample than it is in untreated "A"-fraction (discussed earlier).

Lime-treated acid-insoluble Fractions "C-R" (Figure 16) — The spectrum of this acid-insoluble fraction of the lime-treated material has several distinctive bands which are not apparent in any of the other samples in the series. These occur at 1160 (strongest band), 1075 (strong), and medium bands at 950, 858, 545, and 524 cm^{-1}. Nearly all of these bands have a well-resolved appearance in contrast to the broad, multicomponent bands which dominate the other spectra.

Above 1200 cm^{-1} the spectrum is somewhat more similar to the spectra of other samples. There is only a very weak shoulder at 1510, possibly suggesting low lignin content (3.4 percent methoxyl), but the other lignin band near 1040 is not visible at all. Again, carboxylate salt is likely since broad absorption is seen at 1565 and 1380 cm^{-1}. The sulfate content is thought to be low due to the limited intensity of the band at 625.

The differences between this fraction and its untreated counterpart are so substantial that it is quite probable that this particular fraction is an artifact. Differences of this magnitude are not evident in any of the other comparisons (in all four series examined under this project) between untreated and lime-treated samples.

Various possibilities were considered to account for this suspected artifact but none are very satisfactory. The spectrum is thought not to be the result of column breakdown (the column is a polyacrylamide) nor does it seem to reflect the presence of silicates.

Untreated and lime-treated acid-soluble Fractions "I + II" (Figure 17) — These acid-soluble fractions show almost identical IR spectra, which are dominated by sulfate peaks. The untreated and lime-treated samples have ash contents of 91 and 79 percent, respectively. The only indications of lignin-related substances are the methoxyl content (0.89 and 0.58 percent) and the shoulder at 1050 cm^{-1}.

Untreated and lime-treated acid-soluble Fractions "III + IV" (Figure 17) — These spectra are also quite closely related. Sulfate content appears to be quite low in both samples. Lignin content appears to be comparable judging from methoxyl contents (4.84 and 4.87 percent) and from the bands at 1570 (shoulder), 1460 (shoulder), 1265, 1215, and 1045. The region between 1400 and 1650 is dominated by the carboxylate bands, with the aromatic ring bands at 1510 and 1460 visible only as shoulders. This contrasts sharply with the lignin-rich untreated and lime-treated Fractions "A" where the ratio of carboxylate bands to aromatic ring bands was much lower.

The only possible effect of lime treatment on the organic systems present may be the inversion of intensities of the lignin-related bands at 1045, 1265, and 1215. In the lime-treated sample the band at 1045 is of lower intensity than the other two bands (at 1265 and 1215).

Pyrolysis gas liquid chromatography — The details of the procedure and conditions are given in the experimental part of this report.

In order to learn more from the small amounts of color bodies available, pyrolysis gas liquid chromatography (GLC) was carried out. Initially

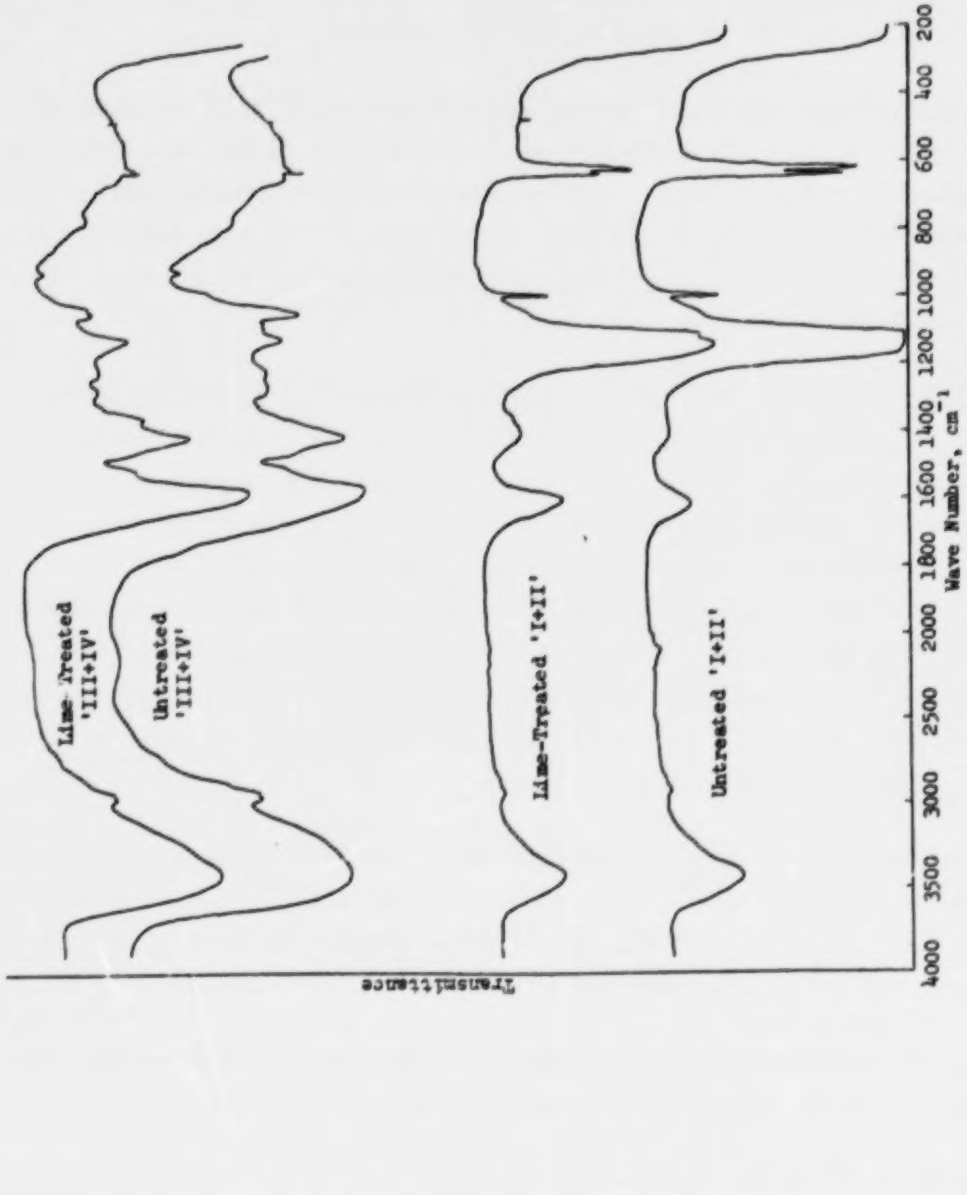

Figure 17. Infrared spectra of untreated and lime-treated acid-soluble color bodies from kraft decker effluent from IPCO

the mass spectrographic identification of the compounds was planned but was not carried out because of lack of time and funds.

Although quantitative analysis of the vapor can be conducted by accurately measuring the area under a GLC peak, only qualitative analysis was carried out in the present work. The chromatograms are given in Figure 18.

The peaks of Indulin-C were identified against known samples[16] and then compared with the decker effluent color bodies. Results are given in Table 13.

Table 13. INDULIN-C PYROLYSIS PRODUCTS

Pyrolysis product peak no.		Identified compound
21		Guaiacol
23		4-Methyl guaiacol (creosol)
28		4-Ethyl guaiacol
29		4-Propyl guaiacol
31		Eugenol guaiacol
31a		4-Vinyl guaiacol
32		cis-isoeugenol
34	Probably	trans-isoeugenol
38		Vanillin

Peaks 10, 12, 17, 21 (guaiacol), and 35 which are quite prominent in the untreated decker effluent are missing in the lime-treated one. The relative ratios of peak heights also seems to have changed during lime-treatment. Peaks 34 and 38 in the untreated and lime-treated chromatograms had retention times similar to that of trans-isoeugenol, and vanillin, respectively.

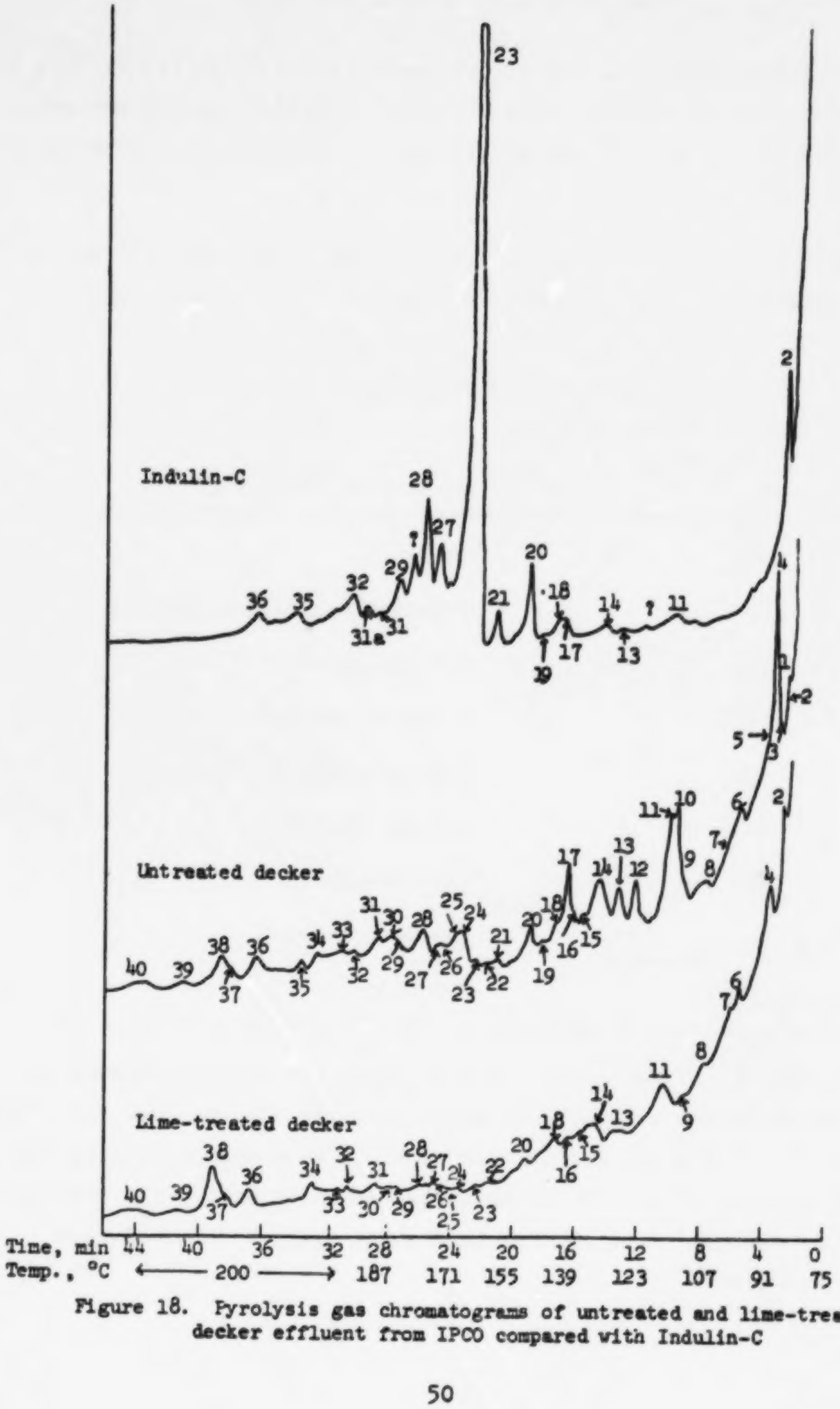

Figure 18. Pyrolysis gas chromatograms of untreated and lime-treated decker effluent from IPCO compared with Indulin-C

Ferulic and vanillic acids upon pyrolysis had the same retention times as eugenol and guaiacol, respectively.

Figure 18 shows that the untreated and lime-treated decker effluents gave somewhat similar chromatograms. A study of such chromatograms as compared to that of Indulin-C suggest that the color bodies in the effluent are degraded lignin fragments.

FURTHER CHARACTERIZATION OF COLOR BODIES FROM KRAFT BLEACH CAUSTIC EXTRACT FROM IPCO

If the pulp is bleached, additional color bodies are solubilized and removed from the pulp. Bleaching at IPCO was accomplished in multistages with most of the color removed in the "Caustic Extraction Stage." Effluent from the caustic extraction stage referred to as "caustic extract" is almost black.

Fractionation of Color Bodies

Acidification —

Acidification was carried out by the same method that was used for the decker effluent and is described in detail in the Experimental part of this report. The results are given in Table 14. The data show that when untreated caustic extract waste was acidified approximately 93 percent color and 79 percent TOC were recovered in acid-insoluble fraction. The acid-soluble fraction contained only 7 percent color and 20 percent TOC. However, when lime-treated waste was acidified the acid-insoluble fraction contained only 37 percent color (1.5 out of 4.0) and 14 percent TOC (2.7 out of 19.6).

The acid-soluble fraction of the lime-treated waste contained about 62.5 percent color and 86 percent TOC. Table 14 further shows that lime treatment removed 98.4 percent color and 96.6 percent TOC of the acid-insoluble fraction and only 66.7 percent color and 16.8 percent TOC of the acid-soluble color bodies.

Table 14. CHANGE IN SOLIDS ISOLATED FROM IPCO EFFLUENTS DUE TO MASSIVE LIME TREATMENT

Fractions	Untreated caustic waste		Lime-treated caustic waste		Reduction due to lime	
	Color[a] yield, %	TOC[b] yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
Caustic extract	100	100	4.0	19.6	96.0	80.4
Acid-insoluble	92.8	79.3	1.5	2.7	98.4	96.6
Acid-soluble	7.2	20.3	2.5	16.9	66.7	16.8

Yield values basis untreated caustic extract solids.

[a] APHA units, Pt-Co color.
[b] Total organic carbon.

Column chromatography —

Fractionations of acid-insoluble and acid-soluble color bodies of the untreated and lime-treated caustic extract were carried out on Bio Gel P-2, P-60 columns and XAD-8 resin, respectively. The results are given in Tables 15 and 16 (for details see Appendix III).

The results in Table 15 show that in the case of untreated acid-insolubles approximately 77 percent of color (71.6 out of 92.8) and 70 percent TOC (55.7 out of 79.3) were obtained in Fraction "A," whereas after lime-treatment this fraction contained only 16 percent (0.24 out of 1.5) of the lime-treated color and 15 percent TOC. The average color and TOC removed from acid-insolubles by lime were 98.4 and 96.6 percent, respectively (over 99 percent of Fractions "A" and "B" were removed).

Table 16 shows that in the case of untreated acid-solubles approximately 96 percent color and 64 percent TOC were obtained in Fraction IV, whereas lime-treated samples had 76 percent color and 41 percent TOC in Fraction IV. The average color and TOC removed from acid-solubles by lime were 67 percent and 17 percent, respectively.

Table 15. FRACTIONATION OF ACID-INSOLUBLE COLOR BODIES FROM BLEACH CAUSTIC EXTRACT BY COLUMN CHROMATOGRAPHY

Fractions	Untreated acid-insoluble color bodies		Lime-treated acid-insoluble color bodies		Reduction due to lime[d]	
	Color yield, %	TOC yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
Fraction "A" from P-2 through P-60 column						
A_1	2.2	2.6	0.08	0.15	96.4	94.2
A_2 through A_6[a]	69.4	53.7	0.16	0.26	99.8	99.5
Acid-insoluble color bodies through P-2 column						
A	71.6	55.7	0.24	0.41	99.7	99.3
B	13.7	24.6	0.12	0.33	99.1	98.7
C	0.40	0.87	0.06	0.15	85.0	82.7
D through H[b]	7.1	3.8[c]	1.08	1.43[c]	84.8	62.4
Unfractionated acid-insoluble color bodies	92.8	79.3	1.5	2.7	98.4	96.6

Percent yields are calculated on the basis of untreated original waste.

[a] Calculated by difference so that A = (A_1 + A_2 through A_6).

[b] Calculated by difference so that values for unfractionated acid-insoluble color bodies = (A + B + C + D through H).

[c] Total by actual determination.

[d] Values calculated from "yield" data of the solids isolated from untreated and lime-treated effluents.

Characterization of Caustic Extract Fractions from IPCO

To provide sufficient material for chemical analysis some adjacent fractions were combined to give bulky fractions. Thus, Fractions "A" through "A_6" were combined giving "A," "C" through "H" were combined, and out of acid-solubles, Fraction I was used as such and II, III, and IV were combined.

Table 16. FRACTIONATION OF ACID-SOLUBLE COLOR BODIES FROM BLEACH CAUSTIC EXTRACT BY SORPTION ON XAD-8 RESIN

	Untreated acid-soluble color bodies		Lime-treated acid-soluble color bodies		Reduction due to lime[a]	
Fractions	Color yield, %	TOC yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
(Combined II+III+IV)	(7.58)	(15.6)	(2.21)	(9.46)	(70.8)	(39.4)
IV	6.9	13.2	1.9	7.0	72.2	47.0
III	0.36	1.0	0.15	0.76	58.3	24.0
II	0.32	1.4	0.16	1.7	50.0	+
I	0.27	6.6	0.14	7.0	48.1	+
Unfractionated acid-soluble color bodies	7.2	20.7	2.5	16.9	66.7	16.8

Percent yield are calculated on untreated original waste. "+" Values showed an increase.

[a] Values calculated from "yield" data of the solids isolated from untreated and lime-treated effluents.

Visible and UV Spectra —

Visible and UV spectra of all fractions were determined at pH 7.6. Absorptivity values were calculated by dividing absorbance with volatile solids concentration in g/l and the results are plotted in Figures 19, 20, 21, and 22.

Ultraviolet region (Figures 19 and 20) — All samples exhibited an increase in absorptivity as the wavelength decreased and were lower than Indulin-C. Almost all untreated and lime-treated samples showed absorption bands at 280 and 205-210 nm indicating the presence of aromatic compounds (ligninlike). The absorptivity values (in UV region) of acid-insoluble Fractions "A" was reduced, "C-H" was increased and of acid-soluble fractions (I and II + III + IV) remained almost unchanged by lime treatment. Only at wavelengths less than 220 nm, the lime-treated acid-soluble color bodies had noticeably higher absorptivity values than

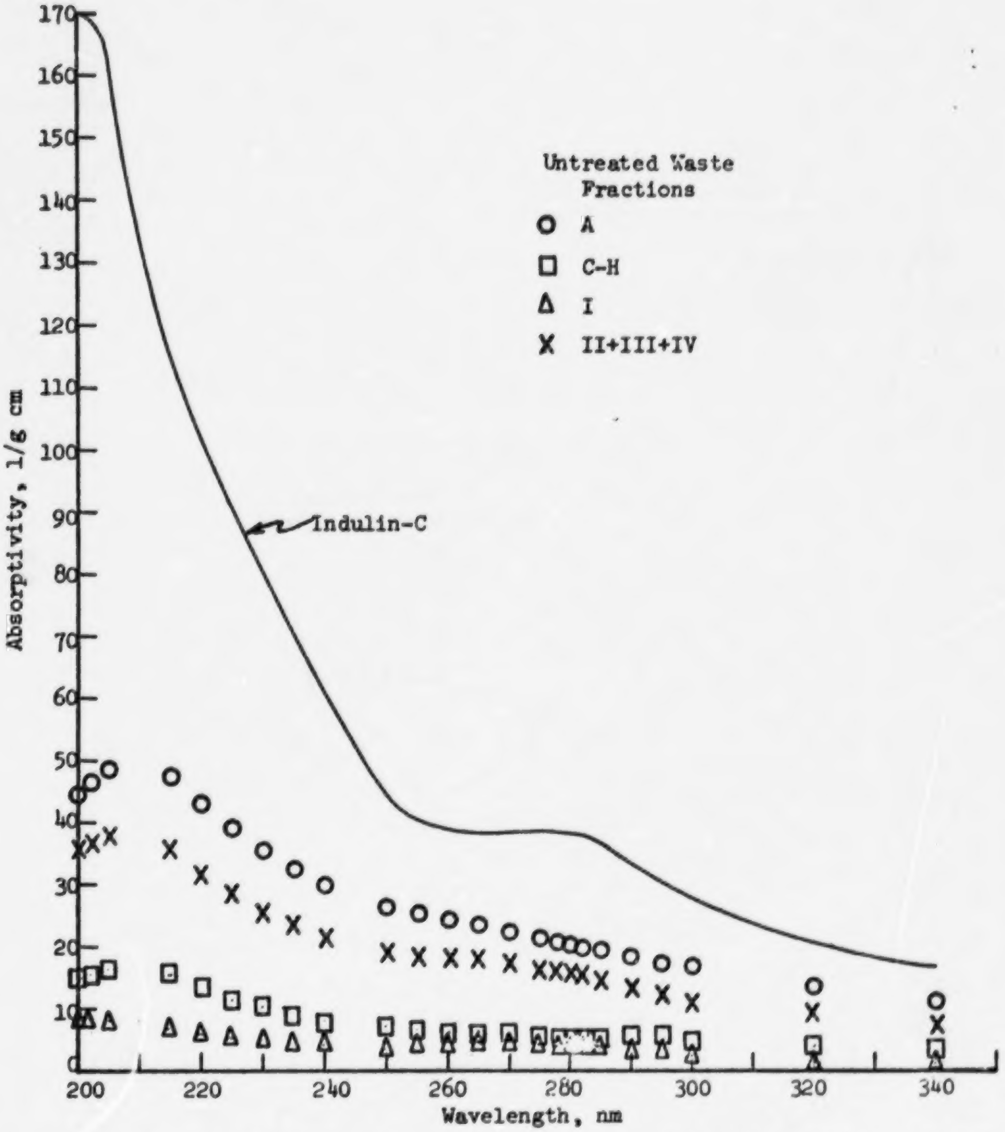

Figure 19. Absorptivity versus wavelength (ultraviolet range) of Indulin-C and untreated kraft bleach caustic extract

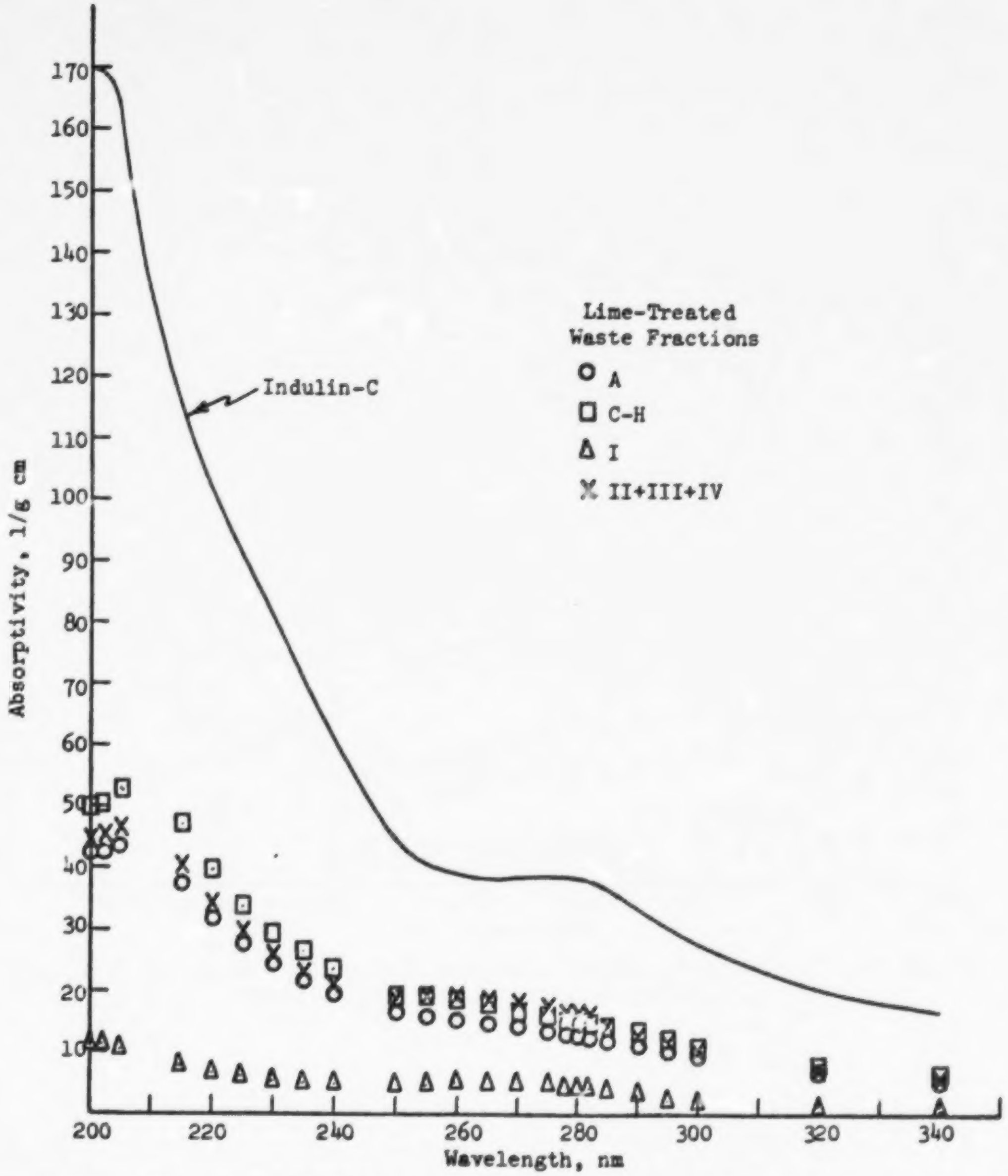

Figure 20. Absorptivity versus wavelength (ultraviolet range) of Indulin-C and lime-treated kraft bleach caustic extract

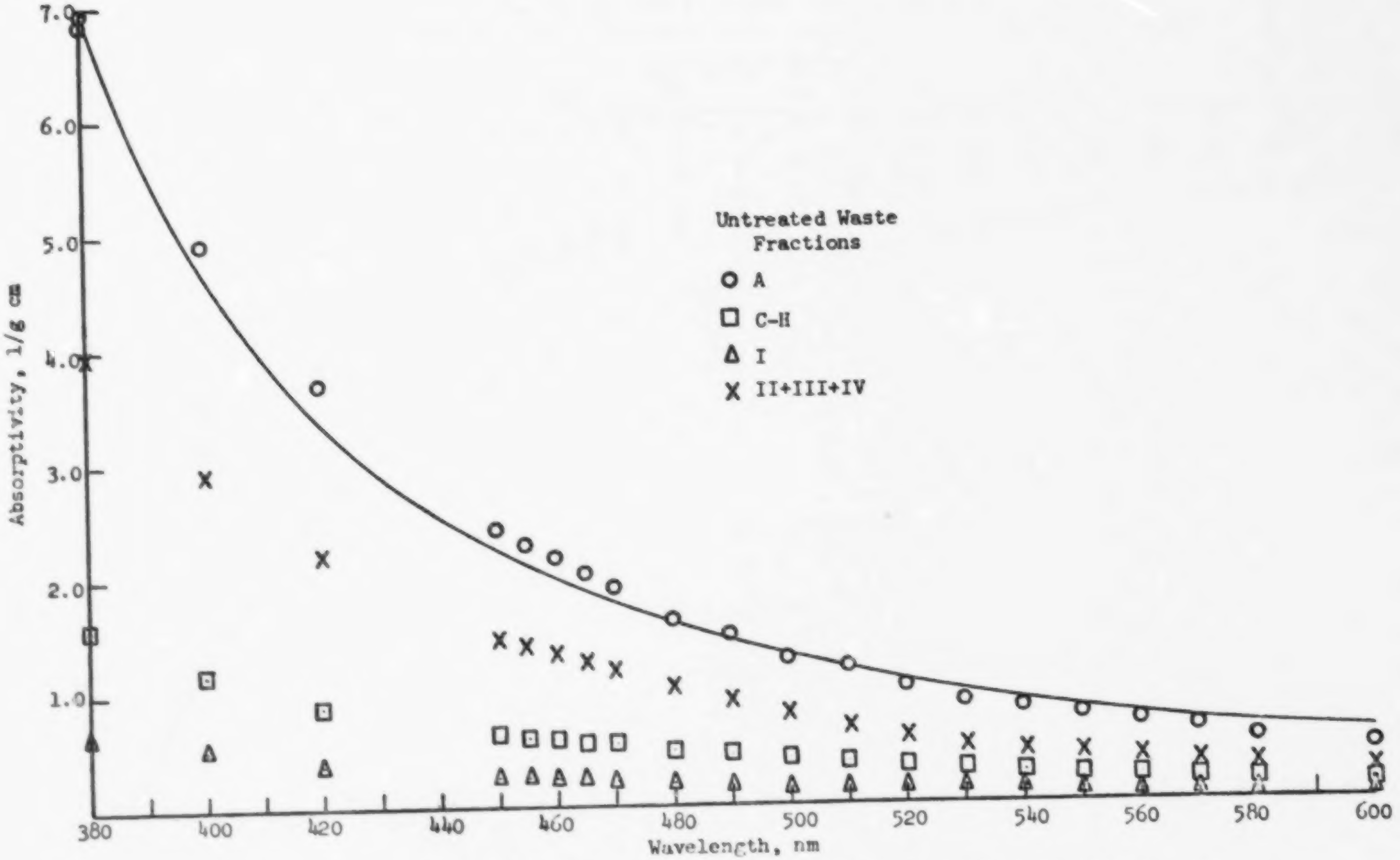

Figure 21. Absorptivity versus wavelength (visible region) of Indulin-C and untreated kraft bleach caustic extract

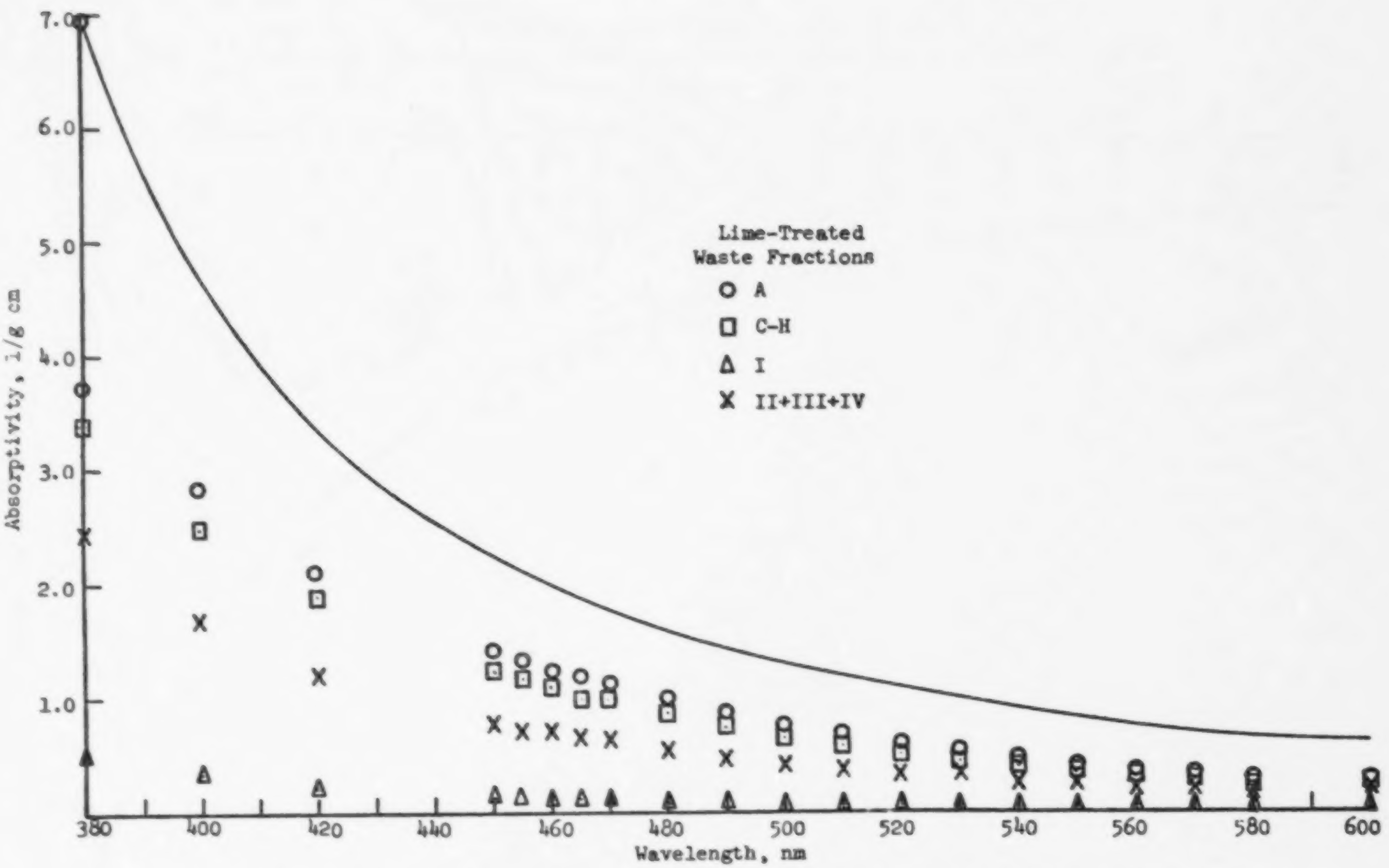

Figure 22. Absorptivity versus wavelength (visible region) of Indulin-C and lime-treated kraft bleach caustic extract

their respective untreated color bodies. This suggests that chromophores which absorb at lower wavelengths, especially below 220 nm, are removed to a lesser degree by lime treatment.

Visible region (Figures 21 and 22) — All samples gave simple absorption curves and exhibited an increase in absorptivity as the wavelength decreased. Fraction "A" of the untreated acid-insoluble color bodies had absorptivity equal to or higher than Indulin-C. Except Fraction C-H all other fractions showed a decrease in absorptivity after lime treatment. A comparison of visible and UV spectra suggests that, although acid-soluble fractions showed no loss in absorptivity in the UV region after lime treatment (in fact an increase in absorptivity was noticed below 220 nm), a definite loss of absorptivity in the visible region occurs, indicating that some color is in fact removed by lime from the acid-soluble fractions.

Molecular Weight Distribution —

Molecular weights of selected fractions of acid-insoluble and all acid-soluble components of the untreated and lime-treated color bodies were determined in a manner similar to that used for the decker effluents. The results are plotted in Figure 23a and b.

Figure 23a suggests that most of the higher molecular weight material is removed by lime. The untreated acid-insoluble color bodies range from M_w 100 to 125,000, whereas the acid-solubles range from M_w 100 to 1100. After lime treatment, however, these values range between < 250 to 9400 and 100 to 450, respectively. Acid-soluble color bodies, Fraction I, had the lowest M_w and acid-insoluble color bodies Fraction "A" the highest. The individual M_w values of acid-insoluble fractions fluctuated somewhat but still a general decrease is noticeable from A_1 to H. These fluctuations could be due to different ash contents of the fractions.

Figure 24 shows that acid-insoluble color bodies having an apparent M_w of less than 400 are not removed by lime treatment. The intermediate range of M_w 400-9500 apparently undergoes partial removal. Over 9500

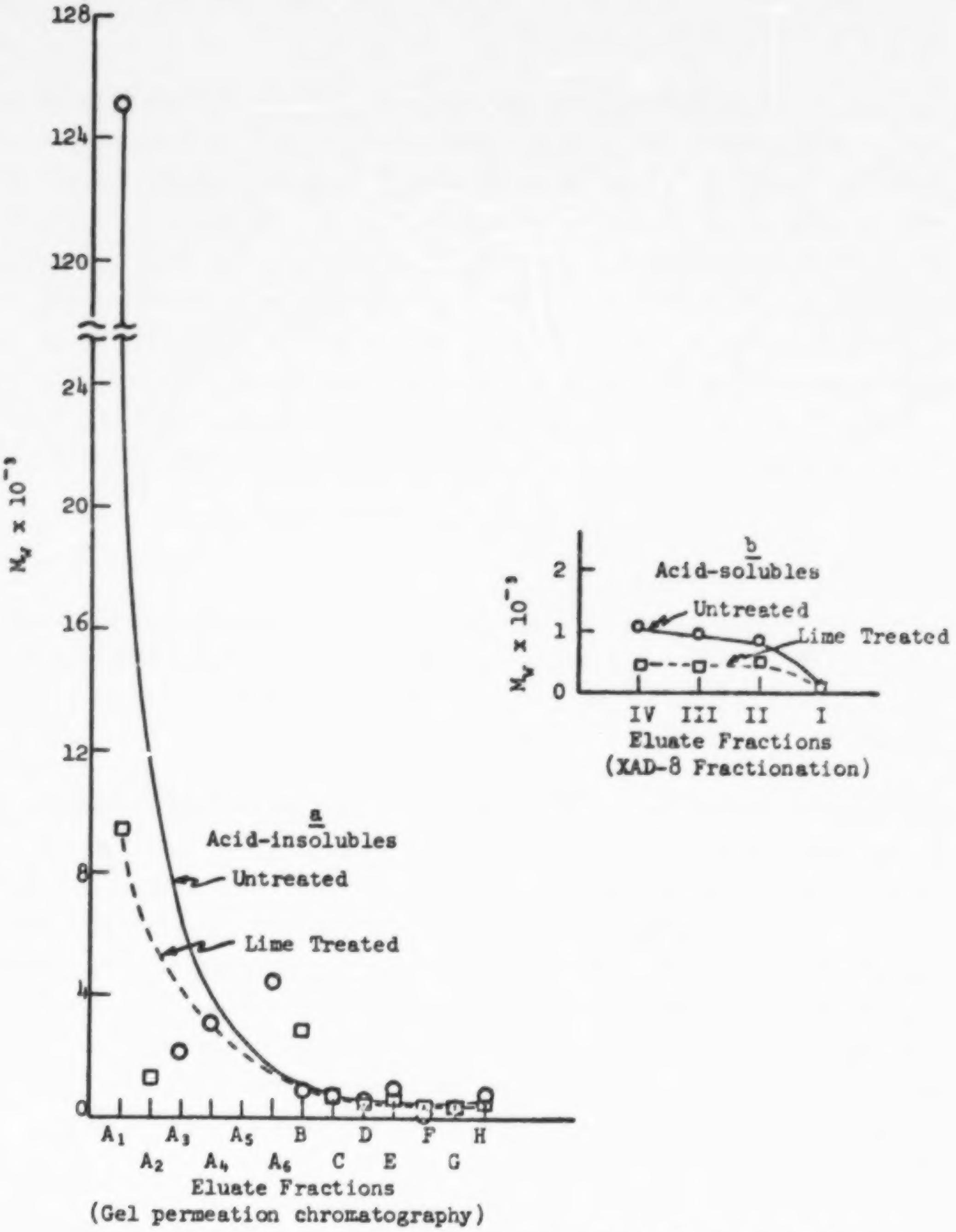

Figure 23. Weight average molecular weight (M_w) distribution of fractionated color bodies from kraft bleach caustic extract from IPCO (M_w at $\omega^2=0$)

complete removal occurred. Over 98 percent removal occurs above a M_w of 1000. The average color and TOC removal of the acid-insoluble fraction was found to be 98.4 and 96.6 percent, respectively (see Table 15).

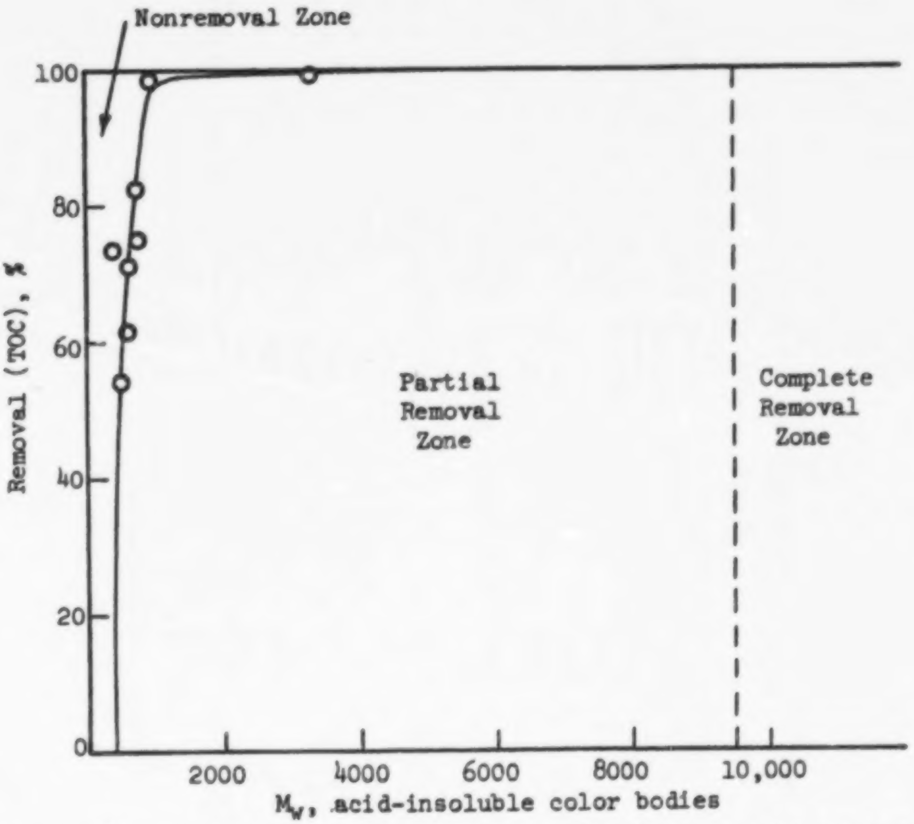

Figure 24. Weight average molecular weight (M_w) of acid-insoluble color bodies from caustic extract versus percentage of removal by massive lime

The acid-soluble color bodies having a M_w of over 500 are removed by lime. The average color and TOC removal of the acid-soluble fractions was found to be 66.7 and 16.8 percent, respectively.

Chemical Characterizations —

The results of the chemical analysis are given in Table 17. The data suggest:

a. The untreated caustic extract contains 0.32 meq phenolic hydroxyls per gram of volatile solids, whereas this

Table 17. ANALYTICAL DATA ON FRACTIONS OF KRAFT BLEACH CAUSTIC EXTRACT FROM IPCO
(Basis o.d. Volatile Solids)

	Indulin-C	Untreated caustic extract					Lime-treated caustic extract				
			Acid-insoluble		Acid-soluble			Acid-insoluble		Acid-soluble	
		Original	A	C-H	II+III+IV	I	Original	A	C-H	II+III+IV	I
Mol. wt. range	--	100-125,000	2,000-125,000	100-1,000	600-1,100	100	100-9,500	1,000-9,500	100-800	400-500	100
Color recovery	--	--	71.6	28.4	96.5	3.5	--	16.0	84.0	88.5	11.5
Ash[a], %	53.8	62.2	23.2	86.64	28.69	83.65	91.80	26.77	67.97	38.82	88.35
Volatile solids, %	46.2	37.8	76.8	13.36	71.31	16.35	8.20	73.23	32.03	61.18	11.65
Phenolic hydroxyl meq/g	1.32	0.32	--	--	--	--	0.13	--	--	--	--
Total sugars[c], %	--	4.60	--	--	--	--	3.42	--	--	--	--
Methoxyl (MeO), %	21.05	2.04	1.90	0.62	1.61	0.74	1.71	3.06	3.22	2.71	1.29
E_{420}	3.39	3.88	3.69	0.91	2.23	0.40	0.79	2.11	1.92	1.24	0.27
E_{280}	38.4	19.00	20.61	5.71	15.90	4.16	12.05	13.00	15.29	16.48	4.74
E_{420}/MeO ratio	0.16	1.90	1.94	1.47	1.39	0.54	0.46	0.69	0.60	0.46	0.21
E_{280}/MeO ratio	1.82	9.31	10.84	6.27	9.88	5.62	7.04	4.25	4.75	6.08	3.67
E_{420}/E_{280} ratio	0.088	0.204	0.179	0.159	0.140	0.096	0.067	0.162	0.126	0.075	0.057
E_{465}/E_{600} ratio	3.14	4.44	4.18	3.46	4.64	3.51	3.34	3.87	3.85	3.39	3.33

[a] Ashed at 600°C, 1 hour. Ash calculated on o.d. material.
[b] Volatile solids = 100% ash.
[c] For individual sugars see Appendix II.

E_{280}, E_{420}, E_{465}, and E_{600} are absorptivities at 280, 420, 465 and 600 nm wavelengths.

value drops to 0.13 after lime treatment (59.3 percent reduction).

b. Total sugar content is reduced from 4.6 to 3.42 g/100 g volatile solids (25.5 percent reduction).

c. Methoxyl content of unfractionated color bodies (original) decreases from 2.04 to 1.71 by lime treatment (16.2 percent reduction). However, the fractionated color bodies (Fractions A, C-H, II + III + IV and I) of the lime-treated waste have higher methoxyl per 100 gram volatile solids than the untreated waste indicating a more lignin-like character. Fractionation probably has eliminated some carbon not associated with MeO.

d. Ratios of E_{420}/MeO, E_{280}/MeO and E_{420}/E_{280} suggest that the untreated caustic extract color bodies contain more chromophores which absorb in the visible region than the lime-treated color bodies.

e. Ratios of E_{465}/E_{600} suggest that the untreated caustic extract and its Fractions "A" (acid-insoluble), and II + III + IV (acid-soluble) are more open in structure. In fact, all color bodies have more open structure than Indulin-C.

One noticeable difference between caustic extract and decker wastes is that the lime-treated color fractions of caustic extract contain higher MeO than their untreated counterparts.

Infrared Spectra —

Caustic extract has the lowest lignin content (judged by MeO content and certain IR-bands) compared to decker or NSSC wastes. Lime treatment seems to produce a band at 1723 (or else markedly changes the carboxylate content) which may also be present as a shoulder in spectra of subsequent fractions.

One of the fractions of the untreated caustic extract was found to be composed of ammonium chloride and sodium chloride. Carboxylate bands in the samples which have higher lignin contents are so strong that the aromatic vibrations at 1510 cannot be detected.

Untreated caustic extract (Figure 25) — Strong bands are evident in the OH region (ca. 3400) and in the region where carboxylate salts commonly absorb (1600 and 1380, broad). The presence of lignin is suggested by a weak band at 1040, but the usual obvious lignin band at 1500 is not apparent. That lignin is a very minor component of the sample is further indicated by the methoxyl content of only 2.04 percent.

There are distinct bands at 830, 765, and 700 cm^{-1} which could be partly due to lignin, but this is doubtful since they do not appear in the spectra of subsequent fractions. These bands do appear to show again in the lime-treated sample, but there again they are not evident in any of the fractions resulting from this material. It is interesting to note that the bands at 830 and 700 are also quite evident in the spectra of the untreated and lime-treated decker wastes (Figure 15), but again no sign of these bands is seen in the spectra of either acid-soluble or acid-insoluble fractions.

Lime-treated caustic extract (Figure 25) — The higher ash content (91.8 vs. 62.2 percent) of the lime-treated sample is undoubtedly due to greater carbonate content and somewhat greater sulfate content. The carbonate bands at about 1450 and 890 are quite prominent, although it should be recognized that the former band is broad and contains a component due to carboxylate groups. The other carboxylate band is seen at about 1600. Carbonate bands are not evident in the spectrum of the untreated caustic extract so their appearance is a direct result of the lime treatment. The previously cited bands at 840, 780, and 700 are clearly seen in the lime-treated caustic extract. These latter bands are considerably more intense here relative to the untreated which parallels the increase in ash and decrease in methoxyl contents (1.71 compared to 2.04). This argues against these bands having their origin in lignin. A broad band at 1140 and another band at 625 implicate sulfate as a probable minor component of the sample.

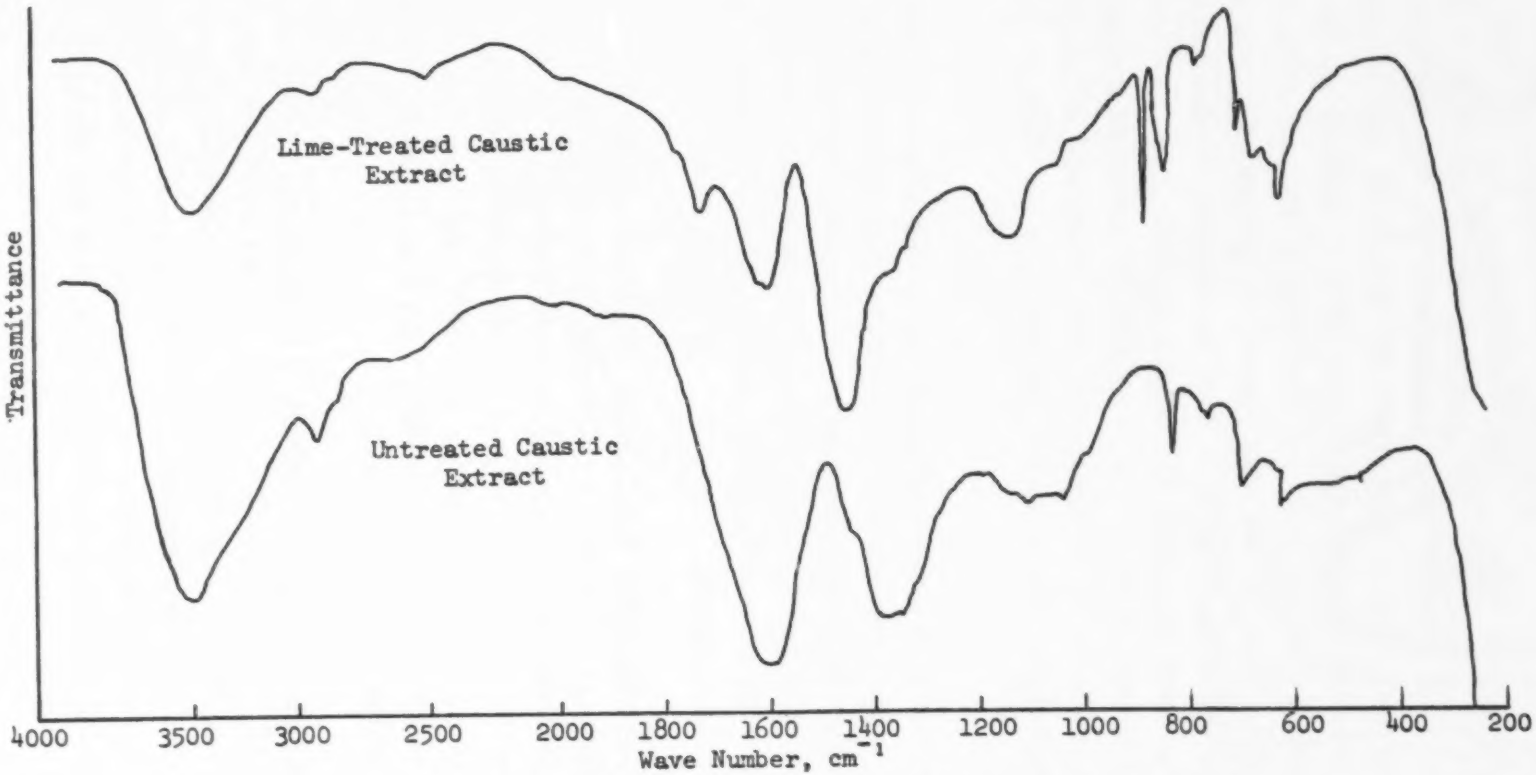

Figure 25. Infrared spectra of untreated and lime-treated color bodies from kraft bleach caustic extract

Lime treatment has apparently produced a carbonyl group in this fraction judging from the new band which appears at 1723. The fractions which result from this lime-treated sample do not contain such a band, although a shoulder in this region is apparent in spectra of lime-treated acid-insoluble fraction "C-H" and acid-soluble fraction II + III + IV; however, such shoulders are also present in spectra of untreated samples. An alternative interpretation is that the carboxylate absorption masks the carbonyl band at 1723 in the untreated sample, but lime treatment causes precipitation of calcium salts rich in carboxylate content. This results in a change in the proportions of carboxylate and carbonyl groups, thus accounting for the different appearance of the spectral region 1550-1750 cm^{-1}.

Neither of the alternative hypotheses can account, however, for the absence of a distinct carbonyl band (rather than a shoulder) in all of the spectra of fractions resulting from the lime-treated caustic extract. Since there is a definite carbonyl band in the original lime-treated sample spectrum, why isn't there a carbonyl band in at least one of the four fractions analyzed?

Untreated acid-insoluble Fraction "A" (Figure 26) — The spectrum of this acid-insoluble fraction is very similar to that of untreated caustic extract. Dominant OH and carboxylate peaks are seen. The band at about 1380 is less broad than is the case in the untreated caustic extract, and peaks at 830, 760, and 700 are not seen. The presence of lignin is indicated by the methoxyl content (1.9 percent) and a band at about 1040 overlapping an adjacent band.

Lime-treated acid-insoluble Fraction "A" (Figure 26) — Again dominant hydroxyl (3420) and carboxylate bands (1570 and 1430) are seen, although the latter are shifted significantly from the corresponding bands in untreated acid-insoluble Fraction "A" and lime-treated caustic extract. Carbonate, which was implicated as a component of the original lime-treated sample, is also seen here (bands at 1430 and 880 cm^{-1}).

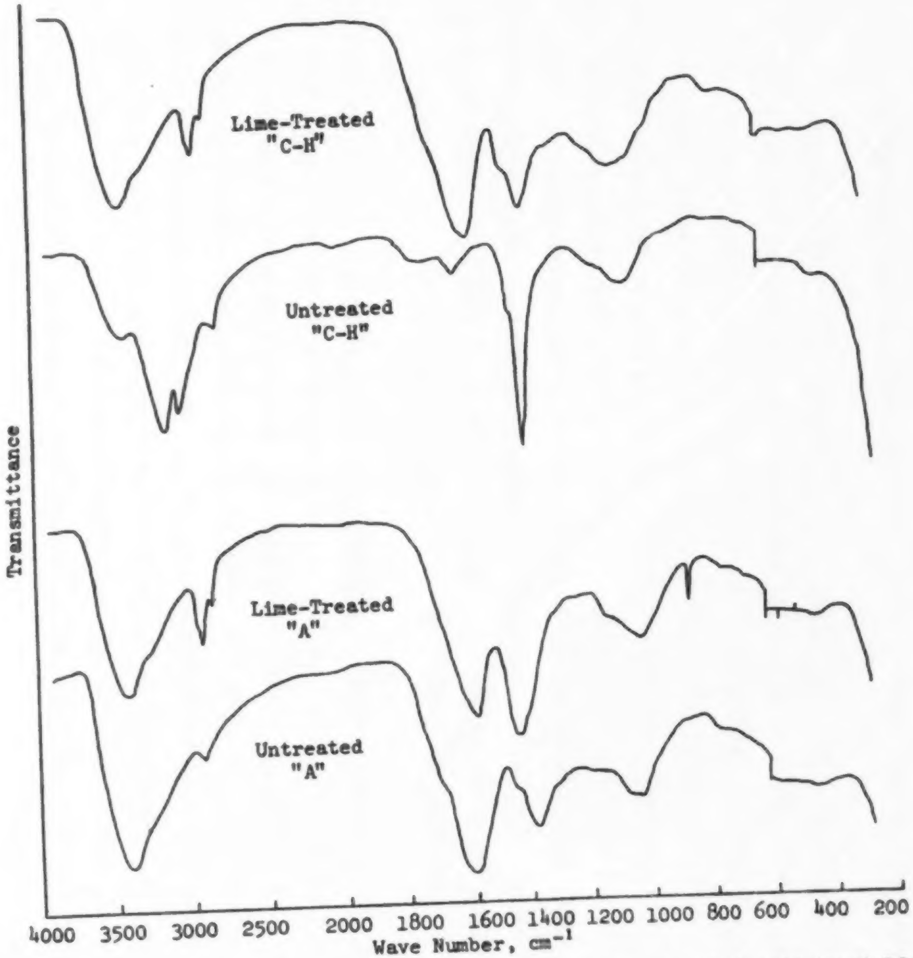

Figure 26. Infrared spectra of untreated and lime-treated acid-insoluble color bodies from kraft bleach caustic extract

One interesting feature of this spectrum is the sharp resolution of the C-H stretching bands. The band components are at 2850, 2925 and a shoulder at 2950. The appearance of this C-H region is like that of the spectra of pure hydrocarbon systems with substantial methyl and methylene content. It is thought that an aliphatic acid salt system (or a mixture of such salts) would best explain the observed C-H stretching bands. In contrast, the C-H band at 2920 for untreated acid-insoluble Fraction "A" is very broad and ill-defined.

A component of the broad band at 1040 is probably due to lignin.

Untreated acid-insoluble Fraction C-H (Figure 26) — This sample is anomalous. The spectrum shows its main bands to be due to ammonium ion: 1400, 2800, 2040, and 3130. X-ray diffraction analysis revealed that this sample is primarily sodium chloride and also contains ammonium chloride. Ammonia may have been generated during a localized degradation (microorganisms?) of the polyacrylamide column; the ammonia in turn could have been neutralized by acid groups to form the ammonium salt. The position of the major bands (listed above) coincides with those observed for known ammonium chloride. Thus, the infared data very strongly support the conclusion that ammonium salts are present.

Lime-treated acid-insoluble Fraction "C-H" (Figure 26) — This spectrum is very similar to that of the lime-treated Fraction "A" except that there is no sign of a carbonate band at 880, and that the maximum at 1435 has shifted in this spectrum to 1400. The latter shift probably also reflects reduced carbonate content. The higher frequency carboxylate band is again near 1575 and the C-H stretching region is well-resolved. The broad absorption centered at 1040 in the lime-treated Fraction "A" now is centered at about 1100, probably indicating higher sulfate content.

Untreated and lime-treated acid-soluble Fractions "I" (Figure 27) — These samples give very similar IR spectra. They are both over 80 percent in ash content. The carboxylate bands show at 1600 and 1400 in both. Both samples apparently contain sulfate (bands at 1130 and 620

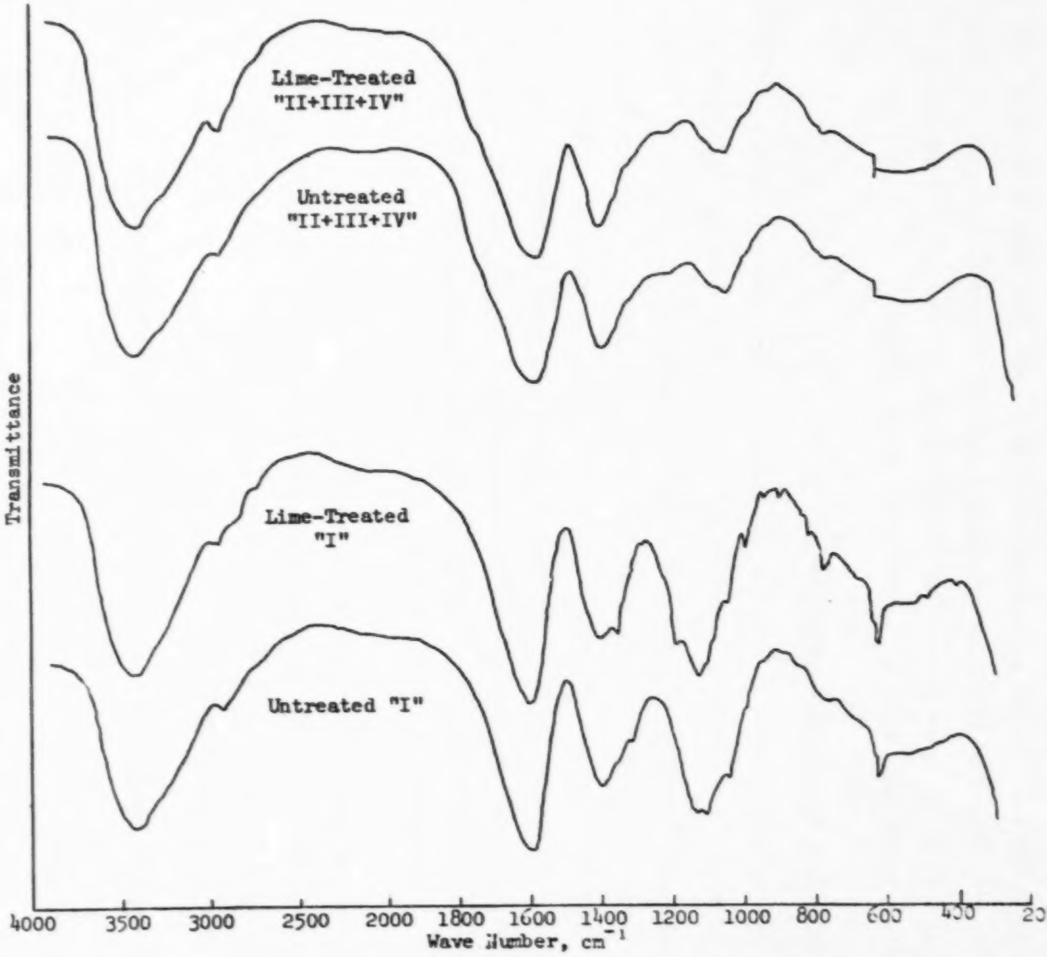

Figure 27. Infrared spectra of untreated and lime-treated acid-soluble color bodies from kraft bleach caustic extract

cm^{-1}). The lime-treated contains bands at 1350 and 1190 not clearly seen in the spectrum of untreated acid-soluble Fraction I. Their origin is uncertain.

Untreated and lime-treated acid-soluble Fractions "II + III + IV" (Figure 27) — These spectra are nearly identical in their appearance. Broad carboxylate bands appear at 1580 and 1390 for the untreated and at 1575 and 1395 for the lime-treated sample. No sulfate or carbonate bands are clearly apparent. The contribution of aromatic rings is only indicated by broad, weak absorption at 1040 cm^{-1}.

Pyrolysis Gas Liquid Chromatography —

Qualitative pyrolysis-GLC was run on all acid-insoluble ("A" and "C-H") and acid-soluble (I and II + III + IV) fractions of the untreated and lime-treated caustic extract. The chromatograms are given in Figures 28-32. Similar peak numbers were allotted to a fraction before and after lime treatment. Therefore, chromatograms in one figure can be compared with one another with respect to their peak members. Chromatograms of the fractions from the same series (i.e., untreated or lime treated) from different figures can only be compared with respect to their retention times and not by peak numbers.

Chromatograms of the untreated fractions in Figures 28, 29, and 30 are almost similar to their lime-treated counterparts but are not identical, indicating that most of the changes occur in these fractions (acid-insolubles) by lime treatment.

Chromatograms of the untreated and lime-treated acid-solubles (Figures 31 and 32) are almost identical, indicating a negligible change due to lime treatment.

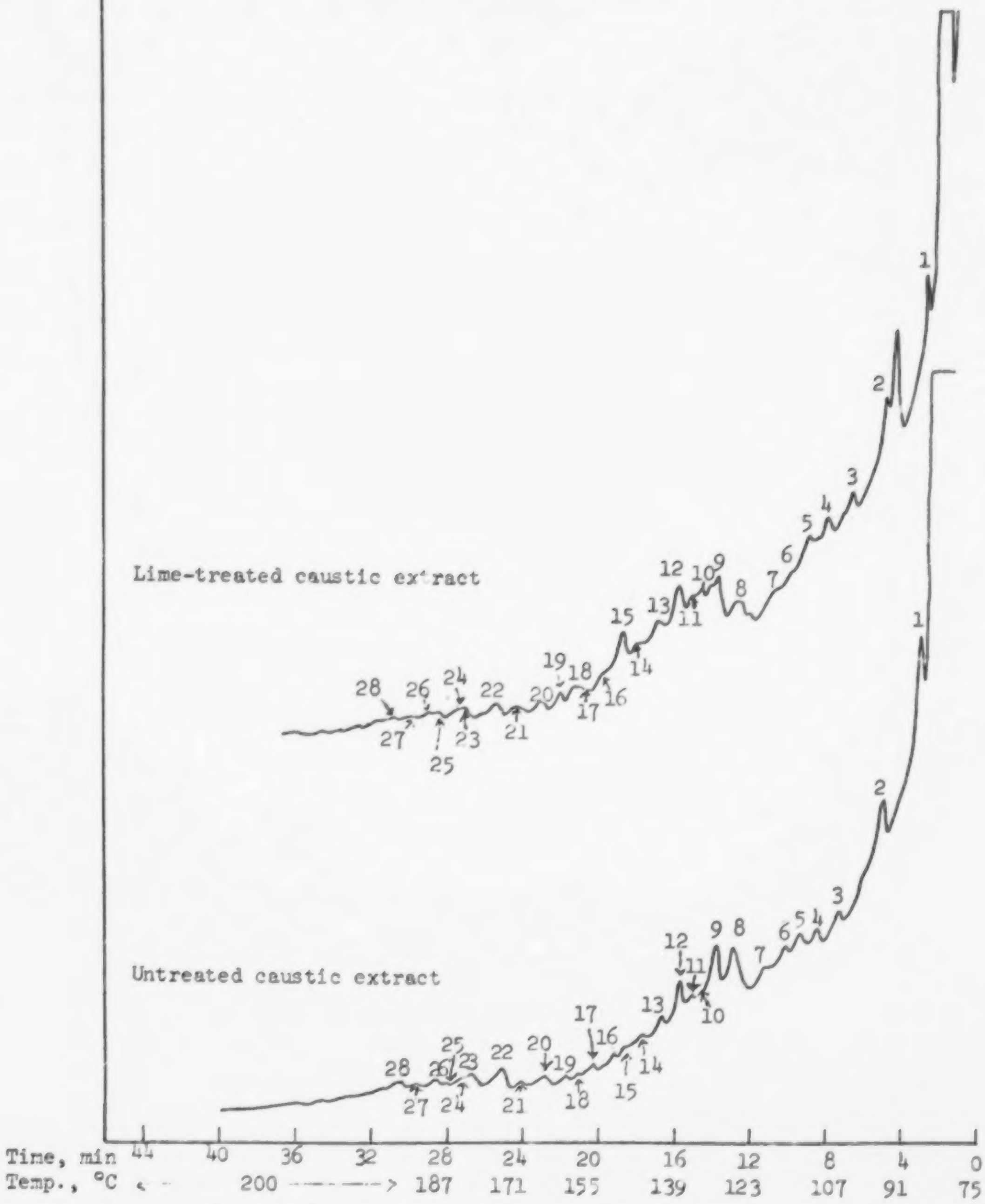

Figure 28. Pyrolysis GLC of untreated and lime-treated kraft bleach caustic extract

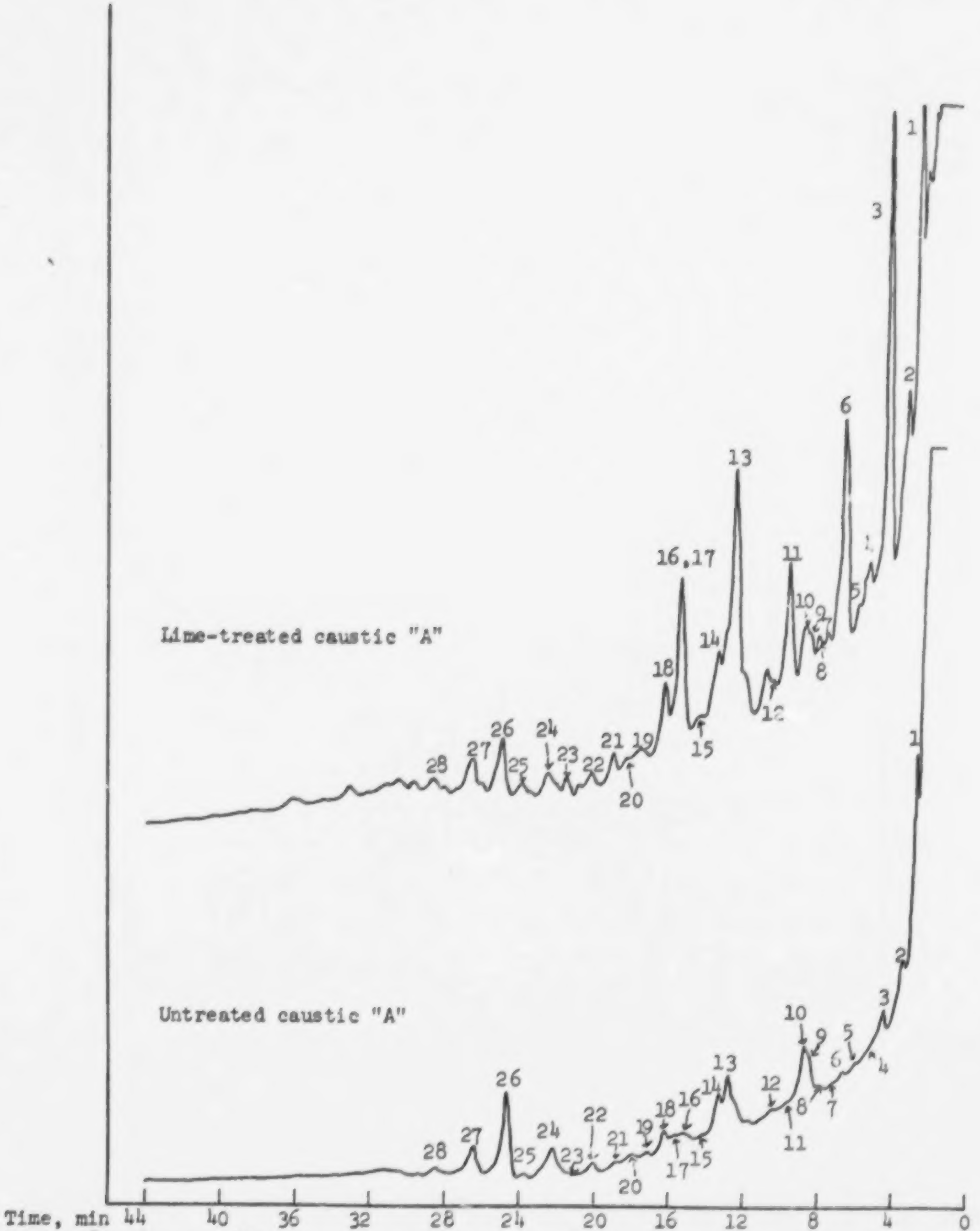

Figure 29. Pyrolysis GLC of untreated and lime-treated acid-insoluble Fractions "A" from kraft bleach caustic extract

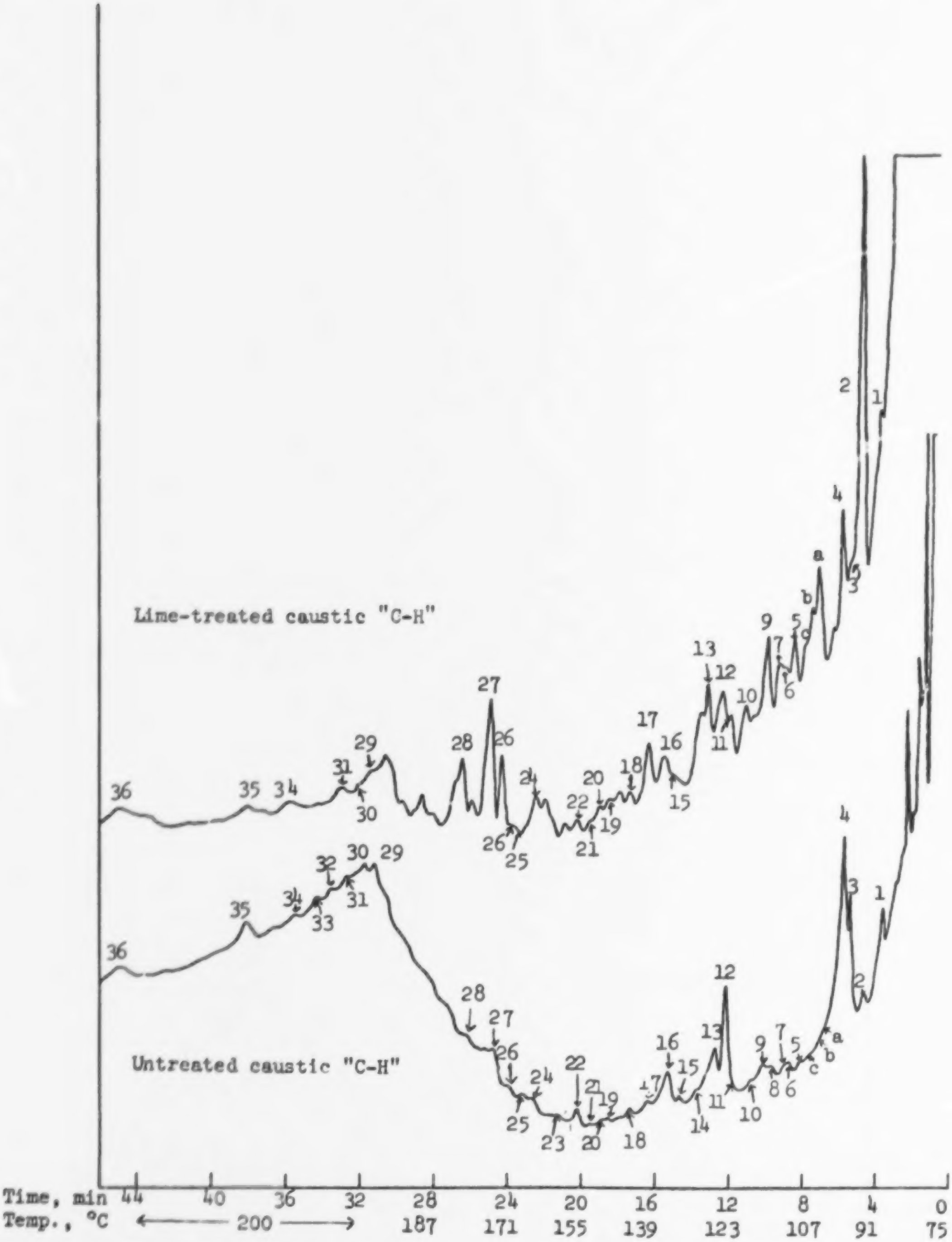

Figure 30. Pyrolysis GLC of untreated and lime-treated acid-insoluble Fractions "C-H" from kraft bleach caustic extract

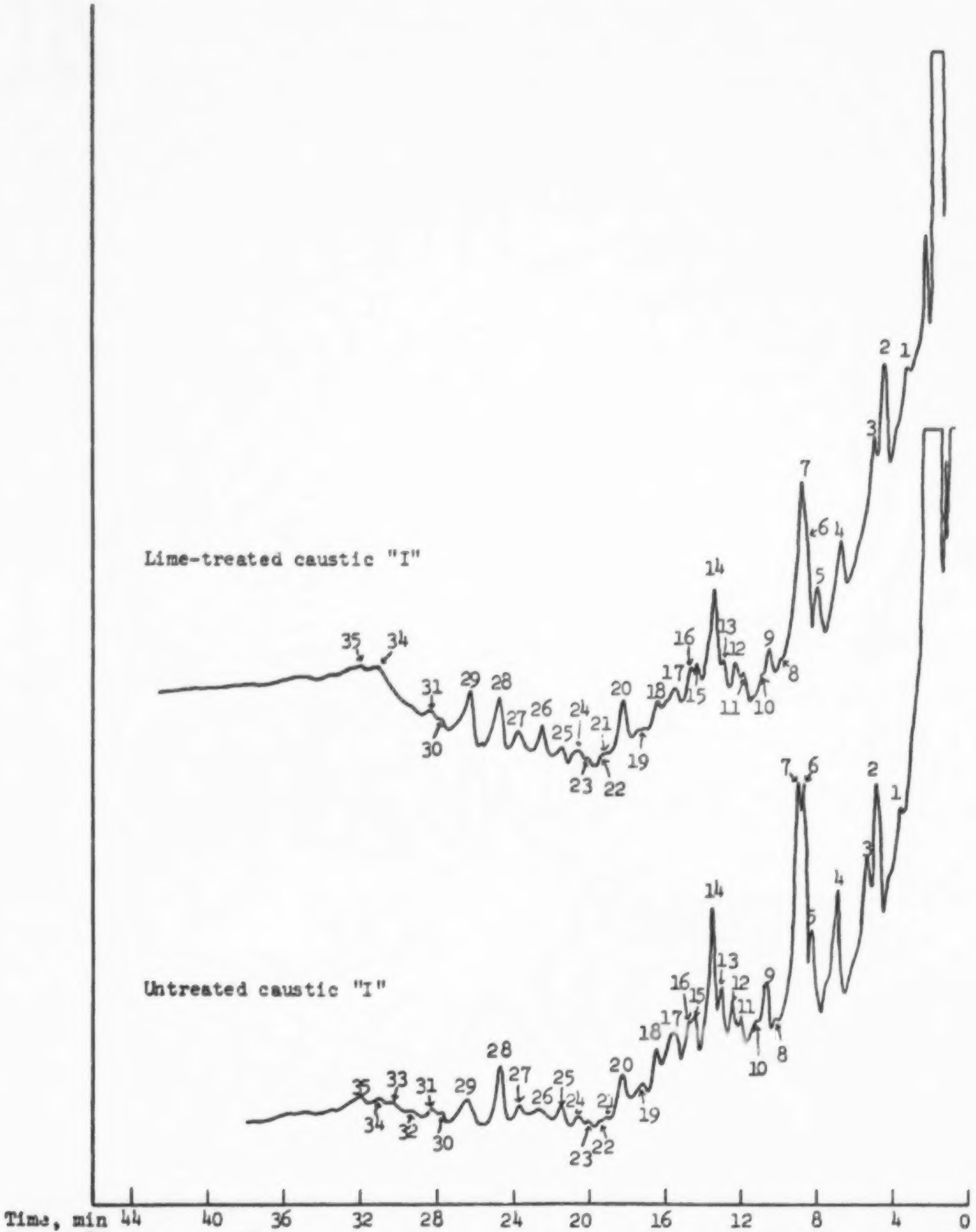

Figure 31. Pyrolysis GLC of untreated and lime-treated acid-soluble Fractions "I" from kraft bleach caustic extract

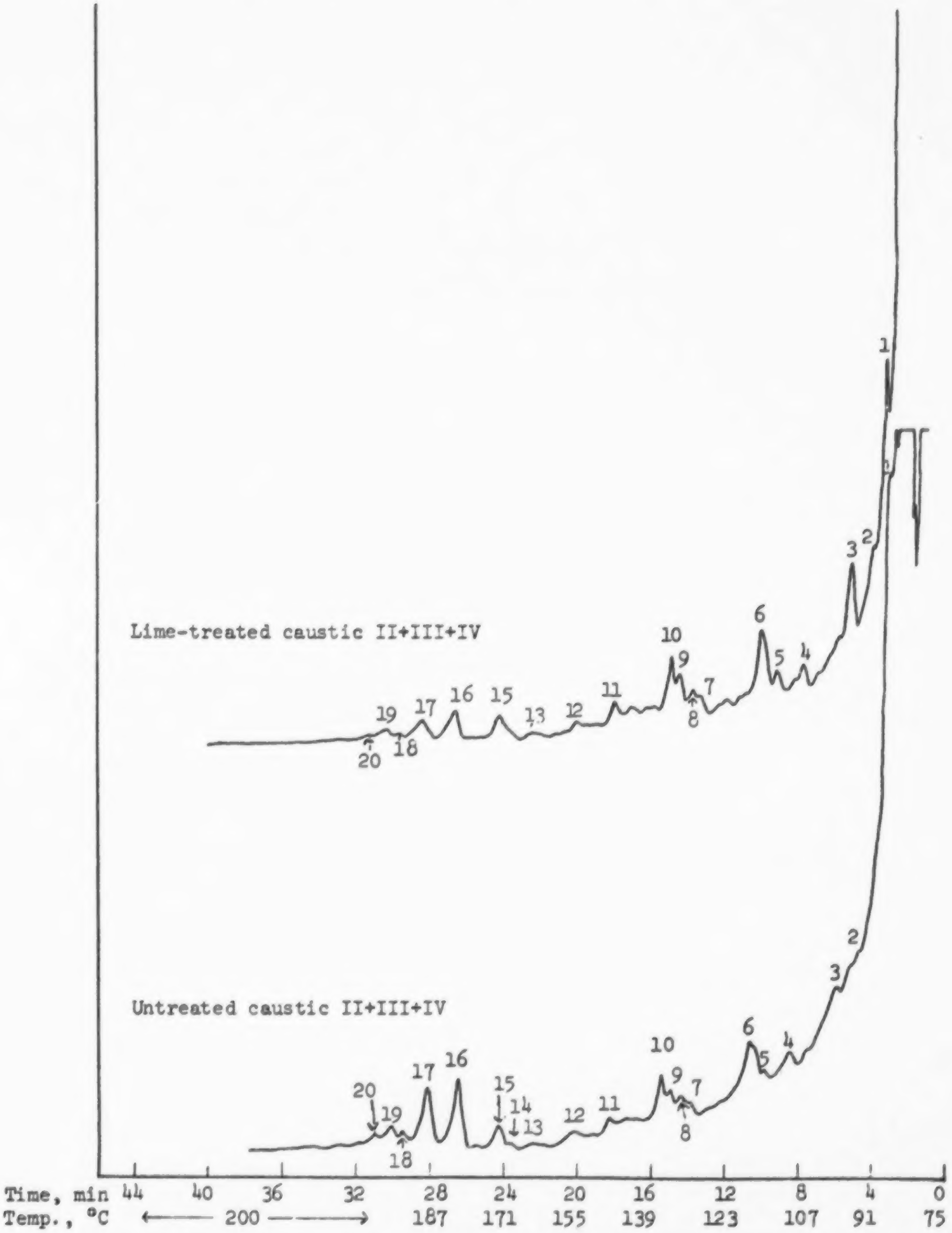

Figure 32. Pyrolysis GLC of untreated and lime-treated acid-soluble Fractions "II+III+IV" from kraft bleach caustic extract

SECTION V

STOICHIOMETRIC LIME TREATMENT
(Continental Can Company, Hodge, Louisiana)

COLLECTION AND PROCESSING OF EFFLUENT SAMPLES

Source of Effluent

Continental Can Company (CONCO) at Hodge, Louisiana is a kraft and neutral sulfite semichemical (NSSC) pulp and paper mill using 88 percent softwood and 12 percent hardwood (total capacity 700 t/day). No multistage bleaching is used. About 300 tons of pulp is bleached by single-stage hypochlorite every two weeks. This is expected to have very little effect on the quality of total effluent[17]. The mill uses well water of low hardness (12-20 ppm).

Mill wastes for the stoichiometric lime treatment included two effluents from pulping and papermaking stages of kraft and NSSC mill. Effluent containing major amounts of wastes from NSSC mill are referred to as NSSC effluent and the other as decker effluent. The total mill effluent volume was 16.5 MGD. Only a portion of this effluent (about 62 percent) was treated. The total mill effluent had a BOD load of 34,000 lb per day and a color of less than 1200 APHA units.

Stoichiometric Lime Process at CONCO

The lime-treatment system initially handled about 10 MGD of mill effluent. Lime concentration ranged from 1300-1500 ppm.

Lime slurry at about 10 percent consistency is injected in the pipe main through which raw effluent is pumped to the color clarifier (135 ft diameter); no mixing device is employed. The clarifier overflow is discharged through submerged orifices into an external collecting channel. Sludge discharge is through 8-inch draw-off piping.

From the color clarifier the effluent passes to a 30 x 12 ft carbonation tank, where lime kiln stack gas is bubbled through the primary color

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clarifier waste. The calcium carbonate formed by carbon dioxide reaction with the remaining calcium hydroxide is settled in a second clarifier substantially identical to the first one. Sludge is withdrawn through a 6-inch pipe.

Fiber losses through the existing mill are 20-25 lb per ton pulp. These fines are allowed to go through the system and seem to help in the settling of lime-color bodies precipitate in the primary clarifier thickener of the lime-treatment system[17].

Combined sludge, withdrawn from the color clarifier, is pumped to a storage tank. Dewatering of the sludge is carried out in a Sharples P-5400 solid-bowl centrifuge operated at 2300 rpm. The cake is discharged to the same kiln feed conveyor which receives the kraft lime and filter cake. The concentrate liquor is returned to the color clarifier to recover residual solids.

The lime kiln is a gas fired unit 12 ft in diameter and 290 ft long. Recovered lime and new lime use are shared impartially between causticizing and effluent treatment.

Effect of Shipment

Two batches each of decker and NSSC effluents were received from Hodge, Louisiana over a period of about five months. Each batch contained separate samples of untreated, lime-treated before carbonation and lime-treated after carbonation stages of the lime treatment plant. All samples were characterized as follows:

Chemical analyses on these effluents (before shipment) were supplied by CONCO and are given in Table 18 (please note the sample code employed as shown in Table 18 footnotes). Aliquots of liquid wastes were also analyzed at the Institute upon receipt and the data were compared with those of CONCO. The results showed that "after shipment" results generally were higher for color and lower for TOC. No definite conclusion could be drawn from the results mainly because this trend was not consistent and differed from sample to sample of the same waste. The

Table 18. CHEMICAL DATA ON EFFLUENTS BEFORE SHIPMENT FROM CONCO

	Decker Effluent						NSSC Effluent					
	Batch 1			Batch 2			Batch 1			Batch 2		
ppm	CCUPP-1	CCLTBC-1	CCLTAC-1	CCUPP-3	CCLTBC-3	CCLTAC-3	CCUS-2	CCLTBC-2	CCLTAC-2	CCUS-4	CCLTBC-4	CCLTAC-4
pH value	9.0	12.3	10.4	9.1	12.1	10.5	8.1	12.1	9.8	7.8	12.2	9.5
Total solids	975	1103	674	1411	2033	1723	2068	2393	1797	1833	2404	1690
Ash[a]	491	908	557	557	664	614	806	1137	802	867	1268	640
Volatile solids[b]	484	195	117	854	1369	1109	1262	1256	995	966	1136	1050
Sodium	163	184	193	242	415	415	299	334	322	310	345	345
Sulfate	224	230	231	325	380	370	310	304	293	180	185	160
Chloride	--	--	17	--	--	17	--	--	14	--	12	--
Color units[c]	685	70	76	980	220	300	2000	820	940	1750	390	500
TOC	202	69	75	294	179	141	521	447	459	672	398	416
BOD	194	135	132	298	284	282	628	637	633	545	463	488

[a] Ashed at 600°C for 1 hour.
[b] Calculated by difference.
[c] APHA color, Pt-Co units.

CONCO = Continental Can Company, Hodge, La.
CCUPP = Untreated decker effluent including paper machine and pulping area wastes from CONCO.
CCUS = Untreated NSSC including kraft decker, paper machine and pulping wastes from CONCO.
CCLTBC = Lime-treated before carbonation from CONCO.
CCLTAC = Lime-treated after carbonation from CONCO.
TOC = Total Organic Carbon.
BOD = Biochemical Oxygen Demand.
1,2,3,4 = Code numbers of the respective effluent samples.

data obtained at the Institute were consistent and could be checked within reason at different times. It was, therefore, concluded that no major change occurred during the shipping (transit) time.

Table 18 shows that the NSSC wastes contain higher color, TOC, BOD, volatile solids, ash, and total solids but lower sulfate content than kraft decker effluent. The data further show that carbonation of lime-treated wastes increased color by 11-14 percent and TOC by 10 percent (only in one case TOC dropped by 20 percent). Similar increase in color and TOC was noticed after carbonation in the case of lime-treated effluents from IPCO (see Table 1).

This increase could be due to the release of chromophores during carbonation which were previously "shielded" by the presence of lime.

Effect of Freeze-Drying and Storage

Changes in sedimentation coefficients before and after freeze-drying of mill effluents were followed for NSSC wastes only. It was expected that kraft decker effluents would behave similar to the ones studied earlier (see Table 2). Results are given in Table 19 which show that the sedimentation coefficient values slightly increase after freeze-drying of NSSC wastes. These increases, however, are not very significant and so it can be said that no appreciable change is occurring in color bodies during freeze-drying.

Table 19. SEDIMENTATION COEFFICIENTS OF NSSC COLOR BODIES

Effluent	Sedimentation coefficients, S[a] Before freeze-drying	 After freeze-drying
Untreated NSSC	0.64	0.84
Lime treated		
before carbonation	0.74	0.75
after carbonation	0.66	0.70

[a] S = Svedberg = 1×10^{-13}.

INITIAL CHARACTERIZATION OF COLOR BODIES FROM THE KRAFT DECKER AND NSSC EFFLUENTS

Chemical Characterization

The results of this analysis are given in Table 20. The data show that freeze-dried NSSC effluents have higher volatile solids, TOC, and much higher amounts of sugars than the decker effluents. Major difference in sugars is due to very high amounts of xylose in NSSC effluents (see Appendix II). Higher sugar content may be the reason for higher BOD values of the NSSC waste.

The ash was analyzed by emission spectroscopy and the metal analysis is given in Table 21. Except calcium and silicon, the amounts of other metals in most of the samples are the same. Substantial differences occur in the amounts of calcium and silicon in similar samples (e.g., Batches 1 and 2 of NSSC or decker effluents). The amounts of silicon and calcium were, therefore, excluded from the total. The data in Table 21 further show that on an average about 65 percent of total metals are removed by lime. However, metal/TOC ratios (see Table 22) of the freeze-dried color bodies from untreated and lime-treated wastes did not change much, suggesting a correlation between the metals and organic carbon and their removal by lime.

Spectrophotometric Examination

Visible and ultraviolet spectra of aqueous solutions of the freeze-dried decker and NSSC wastes (before and after lime treatment) were determined at pH 7.6. Absorptivity values were calculated from these spectra by dividing the absorbance values with the volatile solids in grams per liter. The plots obtained are not shown here. The results showed that:

In the Case of Decker Effluent —

All samples showed simple absorption curves in the visible region; the absorptivity increased as the wavelength decreased. In the ultraviolet region all samples gave absorptivity maxima between 270-280 nm, indicating the presence of ligninlike materials.

Table 20. CHEMICAL DATA ON FREEZE-DRIED WASTES FROM CONTINENTAL CAN COMPANY (CONCO)
(Basis o.d. Material)

	Decker effluent						NSSC effluent					
	Batch 1			Batch 2			Batch 1			Batch 2		
	CCUPP-1	CCLTBC-1	CCLTAC-1	CCUPP-3	CCLTBC-3	CCLTAC-3	CCUS-2	CCLTBC-2	CCLTAC-2	CCUS-4	CCLTBC-4	CCLTAC-4
Yield, g/100 ml	0.06	0.06	0.06	0.11	0.12	0.13	0.18	0.15	0.14	0.16	0.12	0.13
Ash, %	69.1	84.8	85.3	71.8	88.9	85.9	50.4	70.7	71.1	56.6	59.6	76.2
Volatile[a], %	30.9	15.2	14.7	28.2	11.1	14.1	49.6	29.3	28.9	43.4	30.4	23.8
Sulfated ash, %	79.5	96.0	96.9	79.0	102.6	99.6	56.2	65.9	65.4	63.2	76.8	74.0
Sodium, %	22.4	27.4	29.8	20.3	28.0	26.1	14.1	17.1	17.3	19.8	20.6	20.6
Calcium, %	0.39	<0.10	<0.10	0.48	<0.1	<0.1	0.70	<0.1	<0.1	0.36	<0.1	<0.1
Sulfate, %	35.2	37.2	36.8	33.3	30.1	28.2	17.6	20.6	20.3	24.5	24.4	24.0
TOC, %	16.3	8.1	7.6	18.5	7.1	3.7	30.6	24.3	25.8	27.5	19.5	19.3
Total sugars[b], %	5.30	1.18	1.39	2.23	1.07	0.53	8.13	9.13	6.66	6.64	5.05	4.40

[a] Calculated by difference.
[b] For individual sugars see Appendix IV.

For sample code see Table 18.

Table 21. EMISSION SPECTROGRAPHIC ANALYSIS OF FREEZE-DRIED WASTES FROM CONCO
(Basis o.d. Ash)

	Decker effluent						NSSC effluent					
	Batch 1			Batch 2			Batch 1			Batch 2		
Metals, %	CCUPP-1	CCLTBC-1	CCLTAC-1	CCUPP-3	CCLTBC-3	CCLTAC-3	CCUS-2	CCLTBC-2	CCLTAC-2	CCUS-4	CCLTBC-4	CCLTAC-4
Aluminum	0.370	0.150	0.180	0.170	0.079	<0.036	0.24	0.06	0.14	0.22	<0.074	0.088
Barium	0.013	<0.002	<0.002	0.007	<0.002	<0.002	0.012	--	--	0.008	<0.003	<0.003
Boron	0.018	0.016	0.014	0.024	0.018	0.020	0.017	0.016	0.014	0.010	0.010	0.010
Calcium	0.450	0.098	0.089	1.00	0.050	0.052	2.10	0.086	0.080	0.039	0.064	0.070
Copper	0.008	0.003	0.002	0.003	0.002	0.002	0.004	0.003	0.002	0.004	0.003	0.003
Iron	0.086	0.068	0.062	0.076	0.032	0.038	0.092	0.037	0.068	0.060	<0.036	0.038
Magnesium	0.200	<0.022	<0.022	0.160	0.023	0.033	0.180	0.050	0.056	0.160	<0.033	0.037
Manganese	0.054	0.004	0.004	0.031	0.003	0.002	0.074	0.004	0.011	0.038	<0.002	0.003
Silicon	5.4	1.3	0.88	1.10	0.360	0.620	2.20	0.90	1.20	1.34	0.20	0.38
Total[a]	0.75	0.26	0.29	0.47	0.16	0.14	0.62	0.17	0.29	0.50	0.17	0.18

[a] Total does not include calcium and silicon values.
For sample code see Table 18.

Table 22. CHANGE IN METAL/TOC RATIO DURING LIME TREATMENT OF MILL WASTES FROM CONCO

Effluent	Untreated	Lime-treated before carbonation	 after carbonation
Decker effluent			
Batch 1	0.032	0.027	0.033
Batch 2	0.018	0.020	0.032
NSSC-effluent			
Batch 1	0.010	0.005	0.008
Batch 2	0.010	0.005	0.007

All values based on o.d. total solids.

In the Case of NSSC Effluent —

Also single absorption curves were obtained in the visible region. The absorptivity increased as the wavelength decreased.

In the ultraviolet region the absorptivity values of all samples first increased slowly, and then rapidly as the wavelength decreased from 340 to 280 nm. There was little change between 255-280 nm, thus giving a characteristic "shoulder," referred to as maxima. Below 250 nm the absorptivity values increase drastically. Absorptivity values of lime-treated samples were lower than the untreated ones but the nature of the absorptivity curves remained almost the same. This indicated again that the effluents contain materials which show a ligninlike character.

Effect of Lime Treatment

The percentage of color and TOC removal and percentage decrease in absorptivity during lime treatment of the effluents were calculated and the results are given in Table 23.

The results show that generally effluents containing NSSC effluents are not readily decolorized by lime. Lower TOC removal in this case (compared to decrease in absorptivity at 280 nm) may be due to the fact that these effluents contain higher amounts of sugars which resist removal by lime.

Table 23. EFFECT OF LIME TREATMENT ON WASTES FROM CONCO

	Decker effluent	NSSC effluent
Color removal[a], %	79.0	64.0
TOC removal[a], %	50.0	28.0
Decrease in absorptivity[b], %		
at 420 nm	52.3	62.8
at 280 nm	33.0	35.5

Note: Average values from 2 or more samples.

[a] Based on values of effluent samples.

[b] Decrease in absorptivity caused by lime treatment based on volatile solids content isolated from effluents.

Because of lack of material the untreated decker wastes (Batch 1 and 2) were mixed in a ratio of 1:3 and lime-treated decker waste "before carbonation" (Batch 1 and 2) were mixed in a ratio of 1:1. These larger mixed amounts were then used for further fractionation.

FURTHER CHARACTERIZATION OF COLOR BODIES FROM KRAFT DECKER EFFLUENT FROM CONCO

Fractionation of Color Bodies

Acidification –

Concentrated solutions of color bodies were acidified as before and the results are given in Table 24.

The data show that, upon acidification of untreated wastes, 86.5 percent color and 65.8 percent TOC were recovered in the acid-insoluble fraction. The acid-soluble fraction contained only 13.5 percent color and 34.2 percent TOC. The lime-treated wastes upon acidification yielded 61 percent color (12.8 out of 21.0) and 37 percent TOC in the acid-insoluble fraction, and 39 percent color and 63 percent TOC in the acid-soluble.

Table 24. CHANGE IN SOLIDS ISOLATED FROM CONCO EFFLUENTS DUE TO STOICHIOMETRIC LIME TREATMENT (Basis untreated decker solids)

Fractions	Untreated decker waste		Lime-treated decker waste		Reduction due to lime	
	Color[a] yield, %	TOC[b] yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
Decker waste	100	100	21	50	79	50
Acid-insoluble	86.5	65.8	12.8	18.5	85.2	71.9
Acid-soluble	13.5	34.2	8.2	31.5	39.3	8.6

[a] APHA color, Pt-Co units.
[b] Total organic carbon.

Lime treatment removed 85.2 percent color and 71.9 percent TOC from the acid-insoluble fraction and only 39.3 percent color and 8.6 percent TOC from the acid-soluble fraction. In other words color bodies which are not precipitated by acidification to pH 1.0 are removed to a lesser degree by lime than those color bodies which are precipitated by acidification. A comparison of "massive" lime treatment of kraft decker wastes from IPCO (Table 9) and "stoichiometric" lime treatment of kraft decker wastes from CONCO (Table 24) confirms that massive lime treatment has no advantage over the stoichiometric system with respect to the percentage color removal. Slight variations in data are, however, expected as the wastes are from different mills.

Column Chromatography

The acid-insoluble and acid-soluble color bodies were fractionated on Bio Gel columns and XAD-2 resin, respectively. The results are given in Table 25 (for details see Appendix IV). Fraction "A" of the untreated waste contains 64 percent color (55.4 out of 86.5) and 69.5 percent TOC (45.7 our of 65.8) of the acid-insolubles. Whereas this fraction in the lime-treated waste contains only 43 percent color and 16 percent TOC indicating the change in composition taking place during lime-treatment.

The percentage color and TOC removal decreases from Fraction A_1 to J (A_1 has the highest M_w as it is excluded from the P-60 column). The average color and TOC removed by lime were 85.2 and 71.9 percent, respectively.

Table 25. FRACTIONATION OF DECKER ACID-INSOLUBLE COLOR BODIES BY COLUMN CHROMATOGRAPHY

Fractions	Untreated acid-insoluble color bodies		Lime-treated acid-insoluble color bodies		Reduction due to lime[c]	
	Color yield, %	TOC yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
Fraction "A" from P-2 column through P-60						
A_1	22.4	27.4	1.9	1.2	91.5	95.6
A_2 through A_4[a]	33.0	18.3	3.6	1.8	89.1	90.2
Acid-insoluble color bodies through P-2 column						
A	55.4	45.7	5.5	3.0	90.1	93.4
B through E	14.0	14.1	7.6	8.0	45.7	44.4
F through J[b]	7.1	6.0	--	7.5	--	--
Unfractionated acid-insoluble color bodies	86.5	65.8	12.8	18.5	85.2	71.9

Percentages of yield are calculated on the basis of untreated original waste.

[a] Calculated by difference so that values for A = (A_1 + A_2 through A_4).

[b] Calculated by difference so that values for unfractionated acid-insoluble color bodies = (A + B through J).

[c] Values calculated from "yield" data of the solids isolated from untreated and lime-treated effluents.

The acid-solubles were fractionated on XAD-8 resin and results are given in Table 26. The data show that the untreated fraction "III + IV" contained 59 percent color (8 out of 13.5) and 31 percent TOC of the acid-soluble color bodies. The same fraction after lime-treatment contained 54 percent color and 31 percent TOC of the lime-treated acid-solubles, indicating that lime-treatment does not appreciably change the color and TOC composition of the acid-soluble color bodies. The table further shows that average color and TOC removed by lime from these color bodies were 39 percent and 9 percent, respectively.

Table 26. FRACTIONATION OF DECKER ACID-SOLUBLE COLOR BODIES BY SORPTION ON XAD-8 RESIN

Fractions	Untreated acid-soluble color bodies Color yield, %	 TOC yield, %	Lime-treated acid-soluble color bodies Color yield, %	 TOC yield, %	Reduction due to lime[a] Color, %	 TOC, %
III + IV	8.0	10.7	4.4	9.9	45.0	7.5
I + II	4.2	17.1	2.4	17.9	42.8	--
Unfractionated acid-soluble color bodies	13.5	34.2	8.2	31.5	39.3	8.6

Percentages of yield are calculated on the basis of untreated original waste.

[a] Values calculated from "yield" data of the solids isolated from untreated and lime-treated effluents.

Characterization of Decker Effluent Fractions

Individual fractions were combined, as before, to give larger acid-insoluble fractions "A," C-J, and acid-soluble fractions I + II and III + IV.

Visible and UV Spectra —

Visible and UV spectra of all fractions were determined at pH 7.6. Absorptivity values were calculated by dividing absorbance with volatile solids concentration in g/l and the results are plotted in Figures 33-36.

Ultraviolet region (Figure 33 and 34) — All samples exhibited an increase in absorptivity as the wavelength decreased. A "hump" is also noticed at 280 nm. Except for acid-soluble fractions of both untreated and lime-treated color bodies, all other samples showed a tremendous increase in absorptivity below 250 nm. A comparison of Figures 33 and 34 suggests

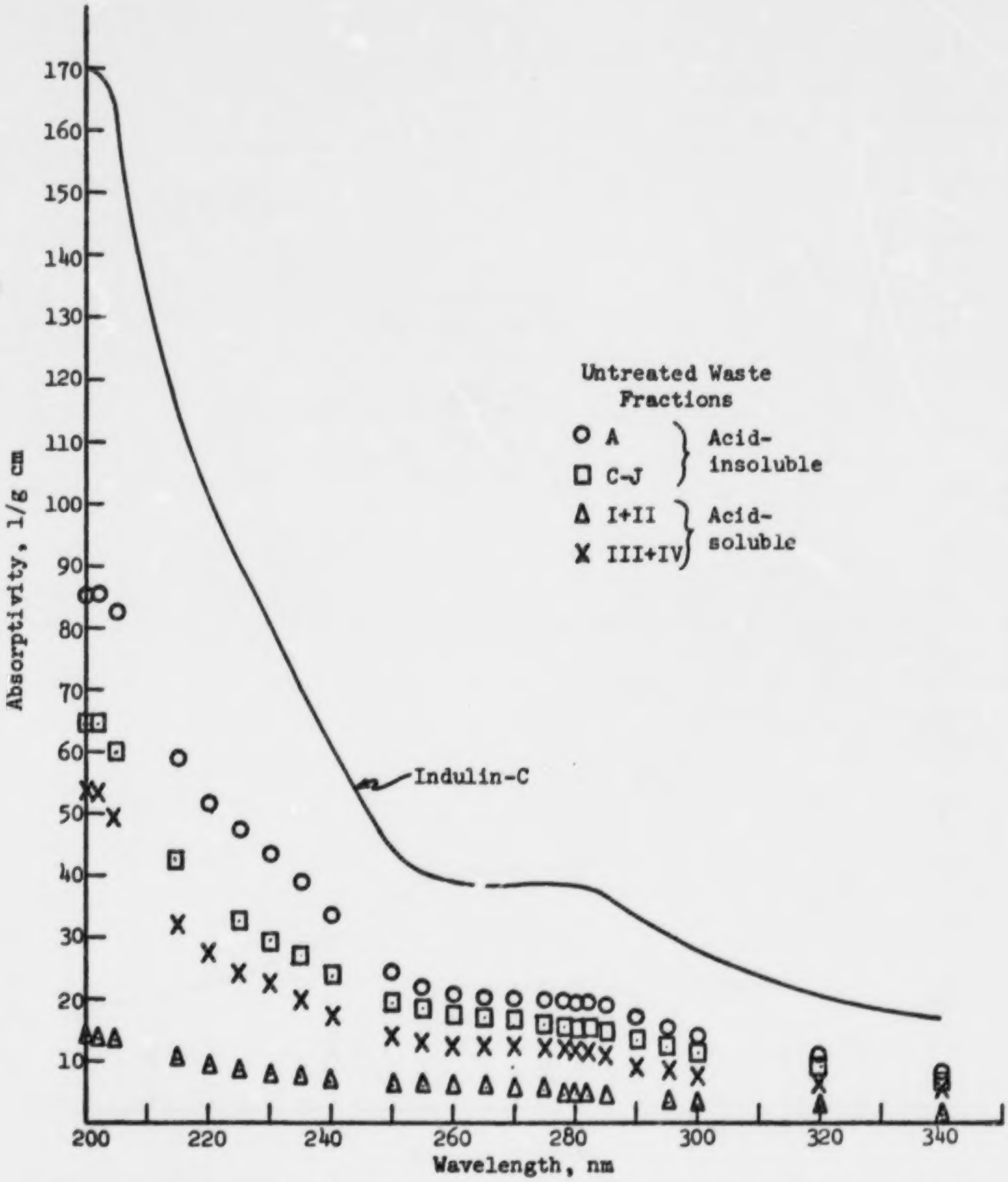

Figure 33. Absorptivity versus wavelength (ultraviolet range) of Indulin-C and untreated kraft decker wastes from CONCO

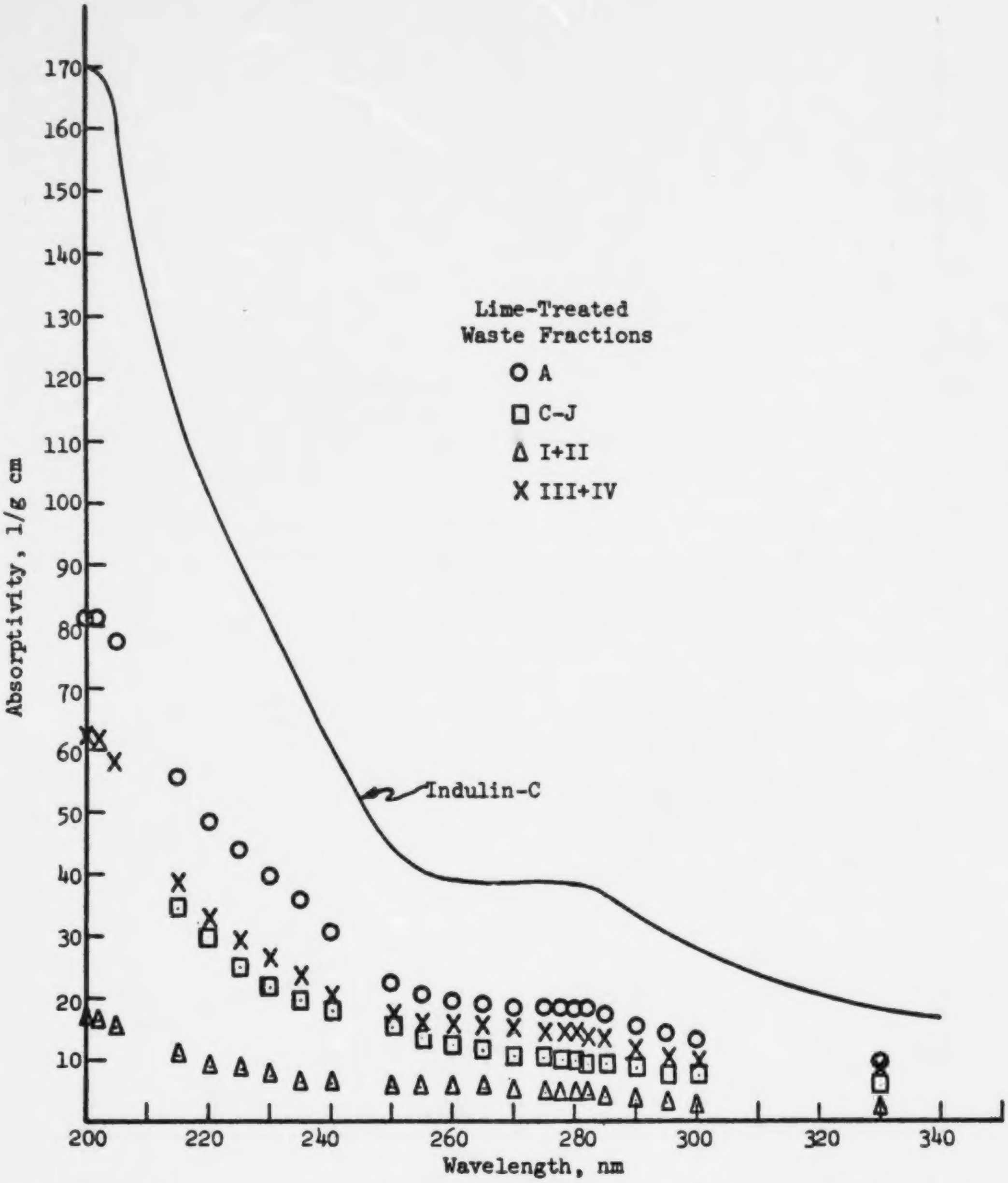

Figure 34. Absorptivity versus wavelength (ultraviolet range) of Indulin-C and lime-treated kraft decker wastes from CONCO

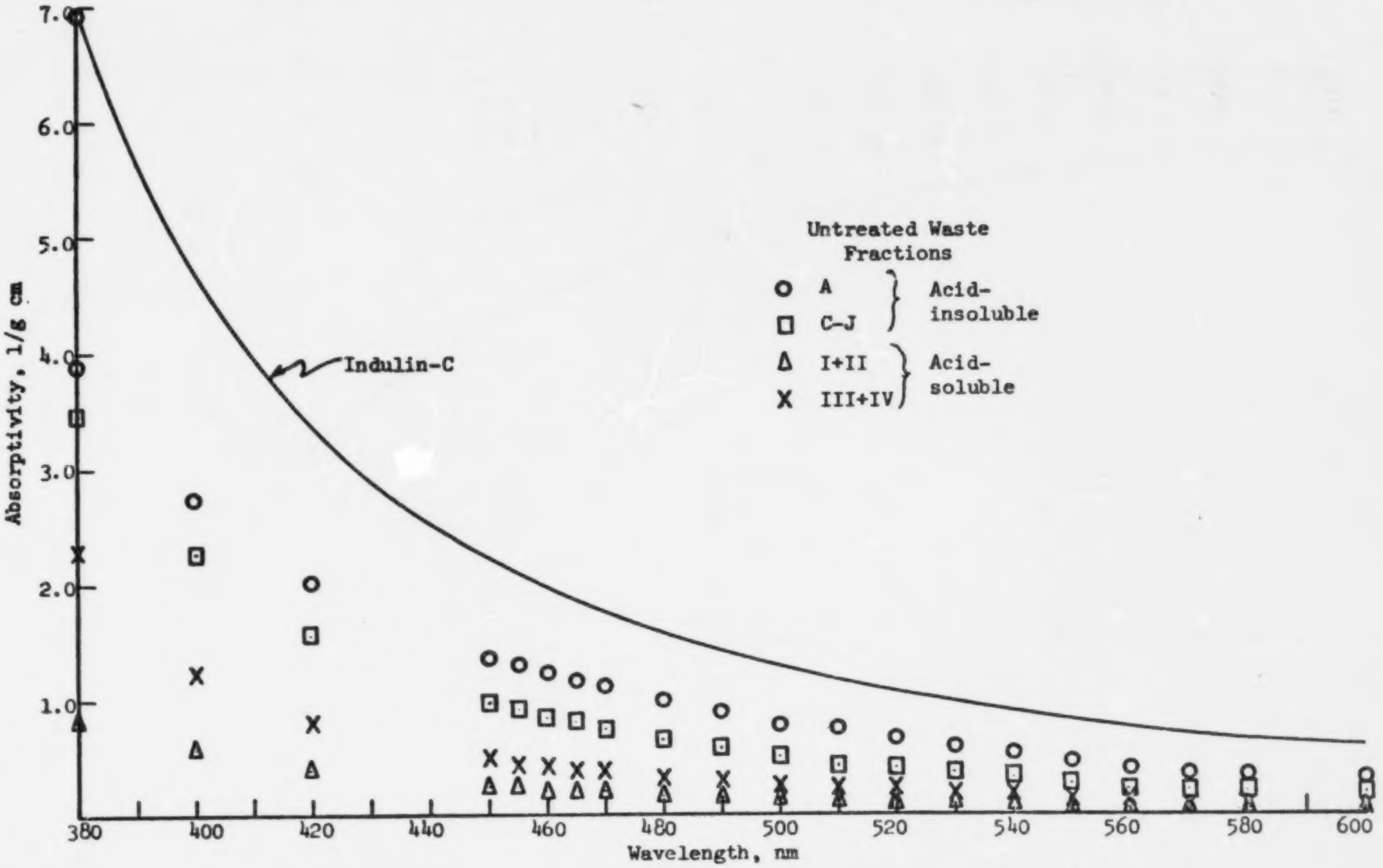

Figure 35. Absorptivity versus wavelength (visible range) of Indulin-C and untreated kraft decker wastes from CONCO

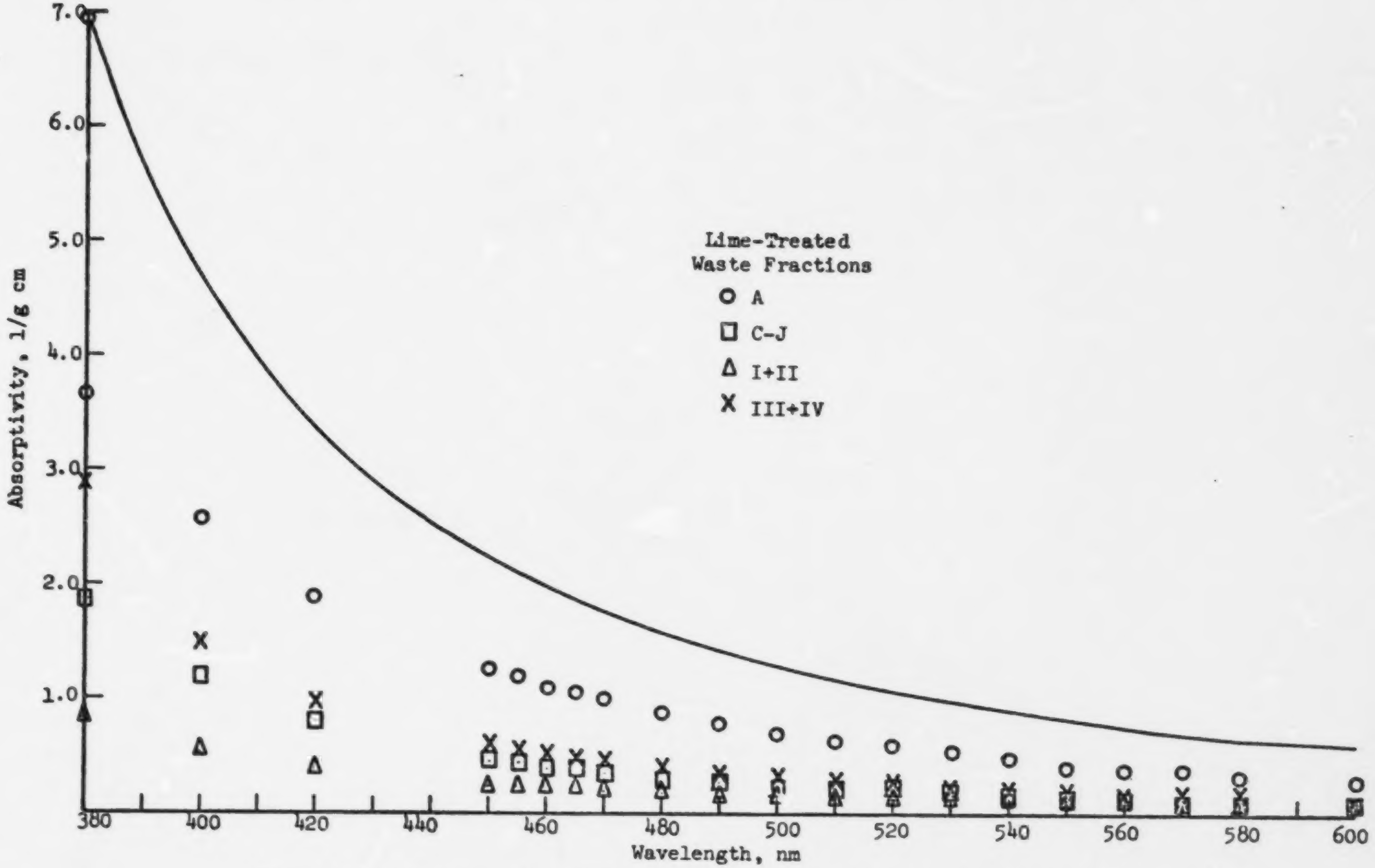

Figure 36. Absorptivity versus wavelength (visible region) of Indulin-C and untreated kraft decker wastes from CONCO

that generally the *acid-insoluble* color bodies (A and C-J) show lower, and *acid-insoluble* color bodies (I + II and III + IV) show the same or higher absorptivity values after lime treatment, indicating that most of the acid-solubles containing UV-chromophores are not removed by lime.

Visible region (Figures 35 and 36) — All samples gave simple absorption curves. Only acid-soluble color bodies, III + IV showed higher absorptivities after lime treatment than the untreated fraction indicating that less color giving carbon is removed from this fraction by lime.

Molecular Weight Distribution —
Molecular weights of the selected fractions of acid-insoluble and all of acid-soluble components of the untreated and lime-treated color bodies were determined as before. The results are plotted in Figures 37a and b.

The data show that acid-insoluble components of the untreated waste are much higher in M_w than those of lime-treated acid-insolubles. The M_w of untreated acid-insoluble color bodies range between approximately 200 to 167,000 whereas after lime-treatment these values drop to < 500 to 42,000 (see Figure 37a).

The M_w of untreated and lime-treated acid-soluble color bodies are quite similar to each other (Figure 37b).

Figure 38 shows that acid-insoluble color bodies having an apparent M_w of less than 500 are not removed by lime-treatment. The intermediate range of M_w 500 to 42,000 apparently undergoes partial removal, and over 42,000 are completely removed. However, about 90 percent removal occurs above a M_w of 2500. It should be mentioned here that M_w of these kraft decker wastes is much higher than kraft decker wastes from another mill (compare Figures 13 and 14 with 37 and 38). As a matter of fact M_w 42,000 for a lime-treated waste is the highest found so far. Not much change is found in M_w of the acid-soluble color bodies after lime-treatment. M_w ranged between 100-550. Maximum removal in these color bodies was about 8.0 percent.

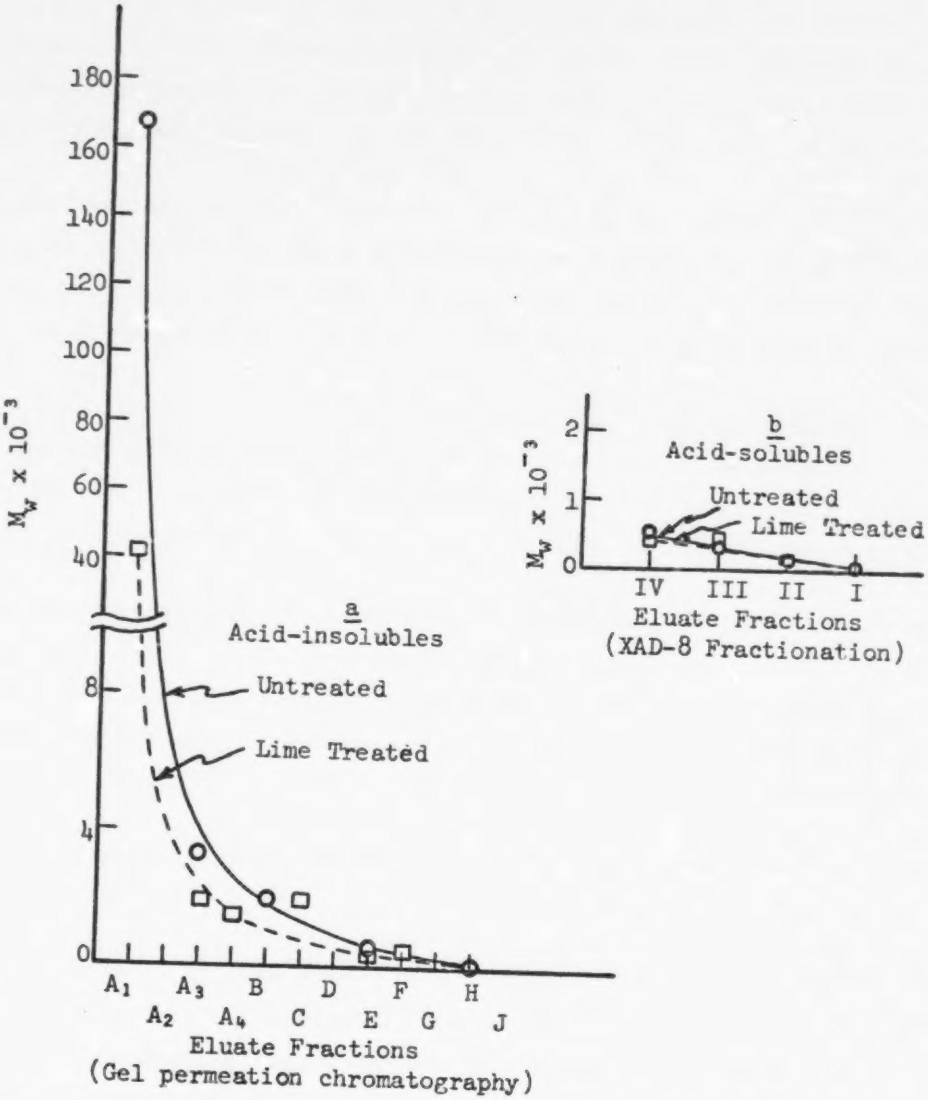

Figure 37. Weight average molecular weight (M_w) distribution of fractionated color bodies from kraft decker effluent from CONCO (M_w at $\omega^2=0$)

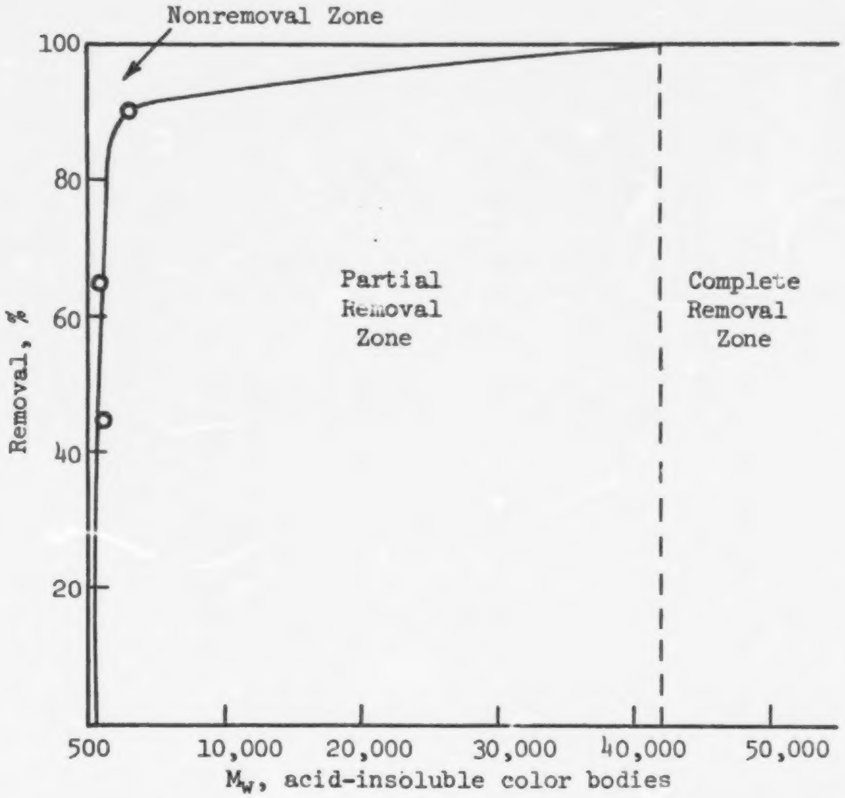

Figure 38. Weight average molecular weight (M_w) of acid-insoluble color bodies from kraft decker effluent versus percentage of removal by stoichiometric lime

Chemical Characterization –

The results of the chemical analysis are given in Table 27. The data suggest:

a. The untreated decker waste contains 0.38 meq phenolic hydroxyls per gram of volatile solids. This value drops to 0.09 after lime treatment, roughly about 76 percent reduction and compares well with the 73 percent reduction observed under the massive lime treatment.
b. Total sugars are reduced from 8.98 to 5.22 g/100 g volatile solids, by lime, a drop of 30.7 percent.
c. Methoxyl content of decker waste is reduced from 5.99 to 3.49 percent (a drop of 41.7 percent). Acid-soluble fraction

Table 27. ANALYTICAL DATA ON FRACTIONS OF DECKER EFFLUENT FROM CONCO
(Basis o.d. Volatile Solids)

	Indulin-C	Untreated decker					Lime-treated decker				
		Original	Acid-insoluble		Acid-soluble		Original	Acid-insoluble		Acid-soluble	
			A	C-J	III + IV	I + II		A	C-J	III + IV	I + II
Mol. wt. range	--	100-167,000	2,000-167,000	180-<2,000	300-550	<100	100-42,000	1,500-42,000	500-<2,000	500-550	<120
Color recovery, %	--	--	64.0	24.6	59.3	31.1	--	43.0	69.5	53.7	29.2
Ash[a], %	53.80	71.11	22.14	70.03	38.53	86.97	86.83	32.71	49.72	35.90	91.24
Volatile solids[b], %	46.20	28.89	77.86	29.97	61.47	13.03	13.17	67.29	50.28	64.10	8.76
Phenolic hydroxyls, meq/g	1.32	0.38	--	--	--	--	0.09	--	--	--	--
Total sugars[c], %	--	8.98	--	--	--	--	6.22	--	--	--	--
Methoxyl (MeO), %	21.05	5.99	10.80	6.38	5.51	1.46	3.49	8.65	3.42	6.72	1.26
E_{420}	3.9	1.19	2.02	1.57	0.820	0.408	0.568	1.90	0.805	0.985	0.400
E_{280}	38.4	12.36	19.94	15.70	11.89	4.73	8.17	18.42	9.64	14.25	4.53
E_{420}/MeO ratio	0.16	0.20	0.19	0.25	0.15	0.28	0.16	0.22	0.24	0.15	0.32
E_{280}/MeO ratio	1.82	2.06	1.85	2.46	2.16	3.24	2.34	2.13	2.82	2.12	3.60
E_{420}/E_{280} ratio	0.088	0.096	0.101	0.100	0.069	0.086	0.070	0.103	0.084	0.069	0.088
E_{465}/E_{600} ratio	3.14	3.01	3.68	3.86	4.51	3.86	3.01	3.38	3.55	4.20	2.48

[a] Ashed at 600°C, 1 hour. Ash calculated on o.d. material.
[b] Volatile solids = 100 - % ash.
[c] For individual sugars see Appendix II.

E_{280}, E_{420}, E_{465}, and E_{600} are absorptivities at indicated wavelengths.

"I + II" contain the lowest amounts of MeO indicating a least ligninlike character.

d. Ratios, E_{420}/MeO, E_{280}/MeO, and E_{420}/E_{280} indicate that except for some greater loss in MeO, the color bodies are quite similar to the lignins in Indulin-C.

e. Higher ratios of E_{465}/E_{600} indicate that acid-soluble fractions III + IV have more open structures than Indulin-C or color bodies of other fractions. In fact Indulin-C contains material with the least open structure.

Infrared Spectra —

The spectra of this series are very similar to the spectra (of comparable fractions) which were discussed for the decker wastes from IPCO (Figures 15-17). Lime treatment seems to produce a carbonyl band at 1722, but this cannot be detected in the spectra of any of the subsequent fractions. The fractions richest in lignin are acid-insoluble; acid-soluble fractions have lower lignin contents and much greater carboxylate content relative to aromatic rings.

The interpretation of the spectrum of one particular fraction, lime-treated acid-insoluble fraction "C-J," is uncertain because it contains so many new bands, including bands in the conjugated carbonyl region.

Untreated and lime-treated decker wastes (Figure 39) — These samples give spectra that are very comparable to the two samples in the other decker effluent series (Figure 15). The only obvious change is that the untreated material gives a carboxylate band at 1595 which is more intense than the band at 1425. This is the reverse of the relative intensities of these bands for the other (Figure 15) series. Once again the lime-treated sample shows a weak band in the carbonyl region at 1722.

Untreated and lime-treated acid-insoluble Fractions "A" (Figure 40) — Sulfate and carbonate are more apparent in the lime-treated sample, and the ash content is higher for this sample as well (32.71 percent vs. 22.14 percent). The lime-treated sample shows spectral bands at 700 and 830 which are not seen in the spectrum of the untreated sample.

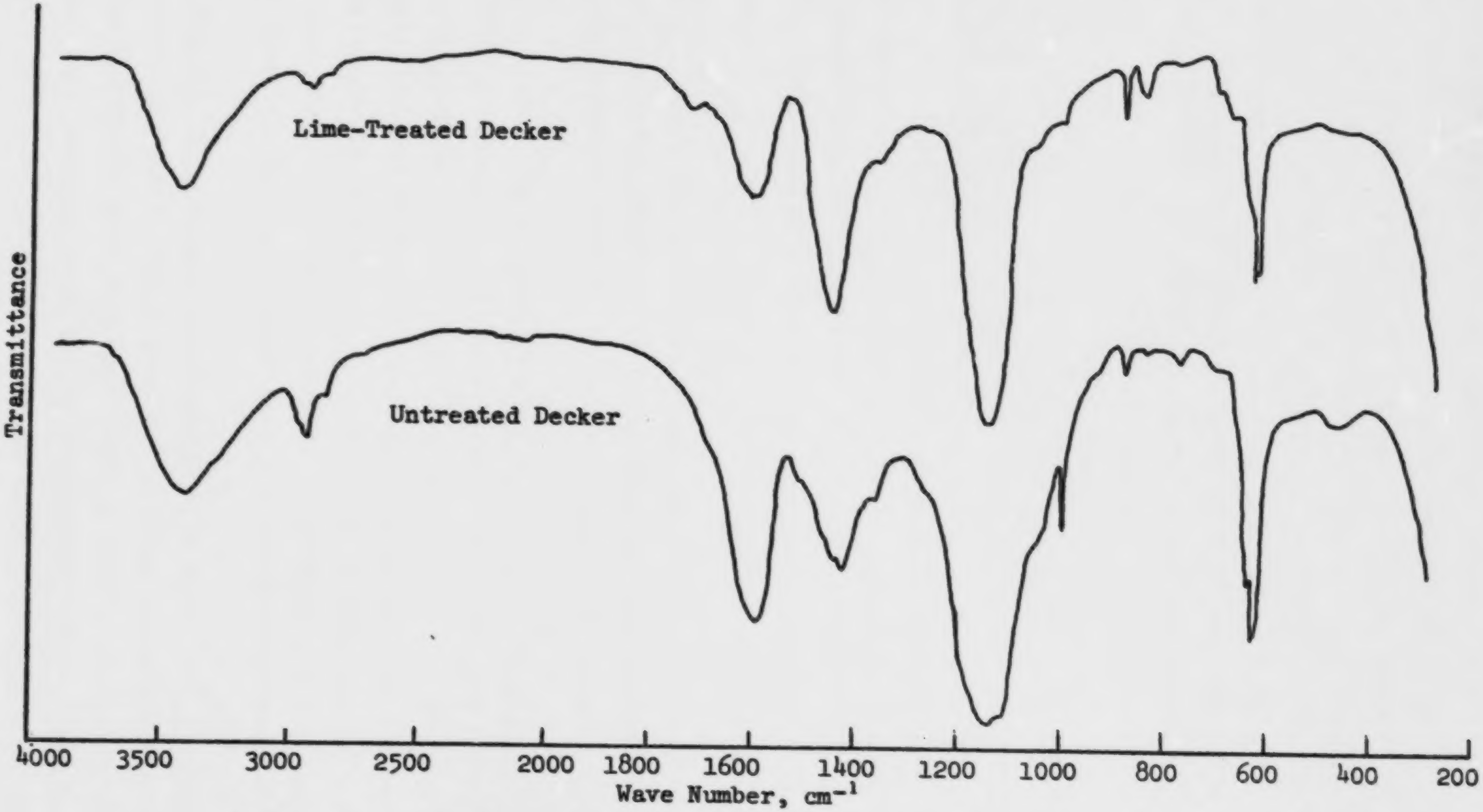

Figure 39. Infrared spectra of untreated and lime-treated color bodies from kraft decker effluent from CONCO

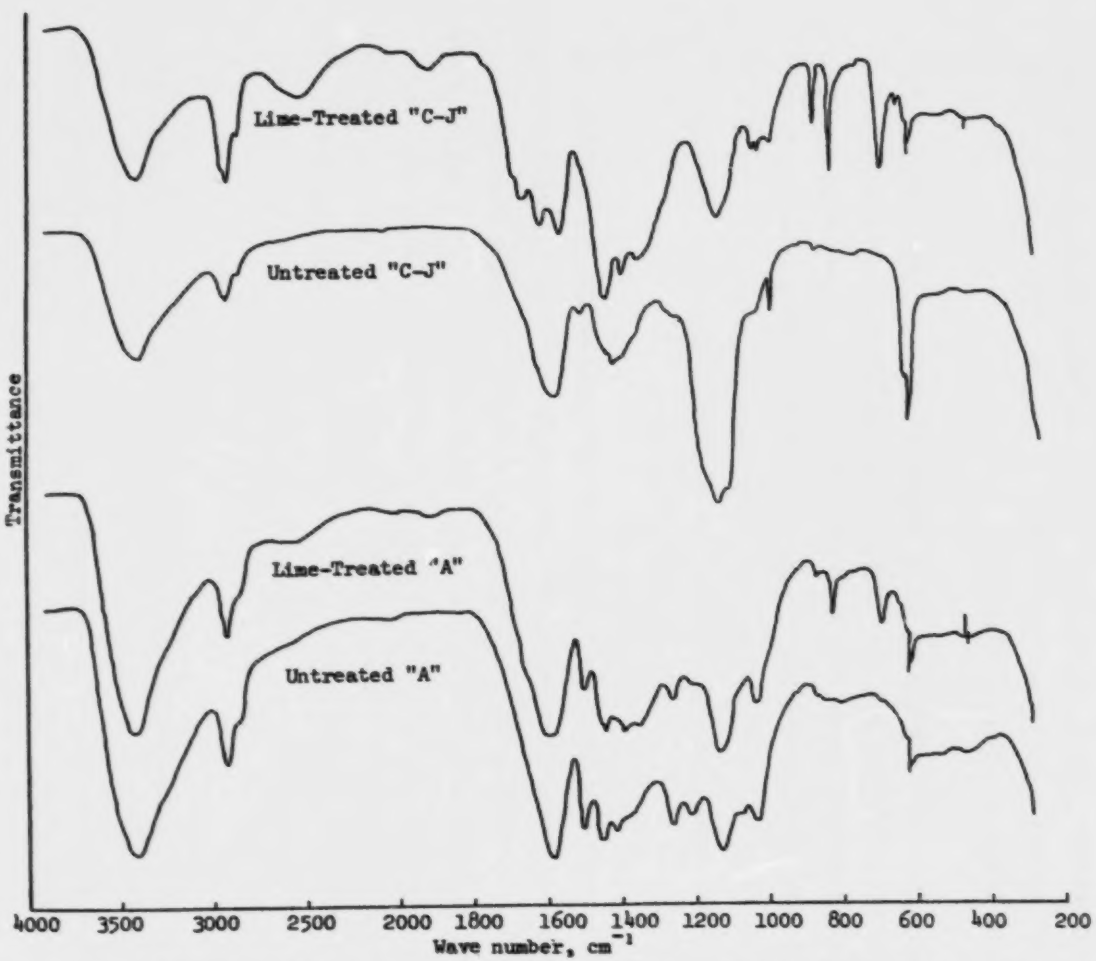

Figure 40. Infrared spectra of untreated and lime-treated acid-insoluble color bodies from kraft decker effluent from CONCO

The bands at 700 and 830 are not seen in the spectrum of the corresponding fraction of the other decker system (Figure 16), although weak bands at this frequency were evident in the original untreated and lime-treated samples.

The lime-treated sample appears to have a somewhat larger carboxylate to aromatic ring ratio than the untreated sample. This parallels the situation found previously (Figure 16).

Untreated and lime-treated acid-insoluble Fractions "C-J" (Figure 40) — The untreated sample spectrum is very similar to the corresponding fraction in the previous series (Figure 16). This lime-treated fraction gives an unusual IR spectrum. The spectrum of lime-treated acid-insoluble fraction "C-R" (Figure 16) was also atypical, but it differs considerably from that of the lime treated acid-insoluble fraction (Figure 40).

In the lime-treated fraction, there are again bands at 700 and 832, as was the case for the lime-treated fraction "A" (Figure 40) just discussed in the previous section. There appears to be a small sulfate content even though ash content is quite high (49.72 percent). The region from 1550-1700 is very unusual; bands are present at 1562, 1615, 1664 and a shoulder at 1690. The latter two frequencies reside in the conjugated carbonyl region. Lignin bands are either very weak or nonexistent. The C-H and O-H absorptions are comparable to those of the other fractions, however.

Untreated and lime-treated acid-soluble Fractions "I + II" (Figure 41) — These spectra are nearly identical and very rich in sulfate (ash contents are 87 and 91 percent). The corresponding fractions in the other decker effluent (Figure 17), gave spectra that are nearly identical with these spectra.

Untreated and lime-treated acid-soluble Fractions III + IV (Figure 41) — These spectra are almost identical. There may be a slightly higher concentration of lignin-related aromatic rings in the lime-treated system;

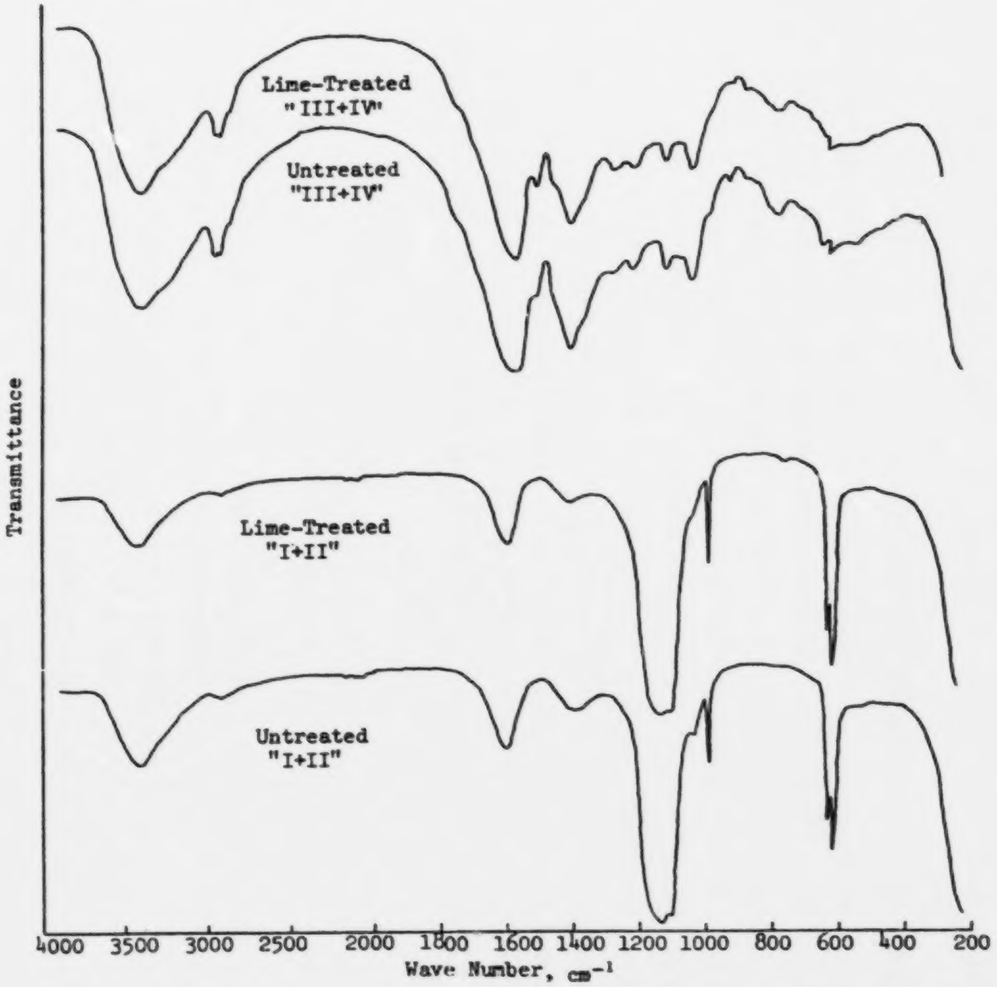

Figure 41. Infrared spectra of untreated and lime-treated acid-soluble color bodies from kraft decker effluent from CONCO

this is based on the higher methoxyl content (6.72 percent vs. 5.51 percent) and the greater prominence of lignin bands at 1510, 1270, and 1045 cm^{-1}.

The region between 1400 and 1650 cm^{-1} is dominated by carboxylate bands. The ratio of carboxylate to aromatic ring absorption is much greater than is the case with the acid-insoluble fractions which also had high lignin content.

Pyrolysis Gas Liquid Chromatography —

Qualitative pyrolysis-GLC was run on untreated and lime treated decker effluent from CONCO. The chromatograms are given in Figure 42. The peak numbers are comparable to those in Figure 18. A comparison of Figure 42 and 18 shows that the color bodies in decker waste from CONCO is more like Indulin-C. Note that peaks 21, 23, 28, 29, 31, 31a, and 32 which have been identified in Indulin-C (Figure 18, Table 13) are also present in CONCO's decker effluent. Lime-treated waste also gives these materials but in lesser relative concentrations. It seems that more degraded and modified color bodies are present in decker effluent from IPCO discussed earlier. Unidentified peaks 36, 38, 39, and 40 are present in both effluents.

FURTHER CHARACTERIZATION OF COLOR BODIES FROM NEUTRAL SULFITE SEMICHEMICAL (NSSC) EFFLUENT FROM CONCO

As has been mentioned earlier, the effluent containing major amounts of wastes from NSSC mills are named as "NSSC-effluent." The minor components of this effluent are other wastes from the pulping and papermaking stage. This is the effluent which is being treated by lime at CONCO's treatment facility at Hodge, Louisiana.

Fractionation of Color Bodies

Acidification —

Acidification of concentrated aqueous solutions was carried out similar to other effluents. The results are given in Table 28. The data show

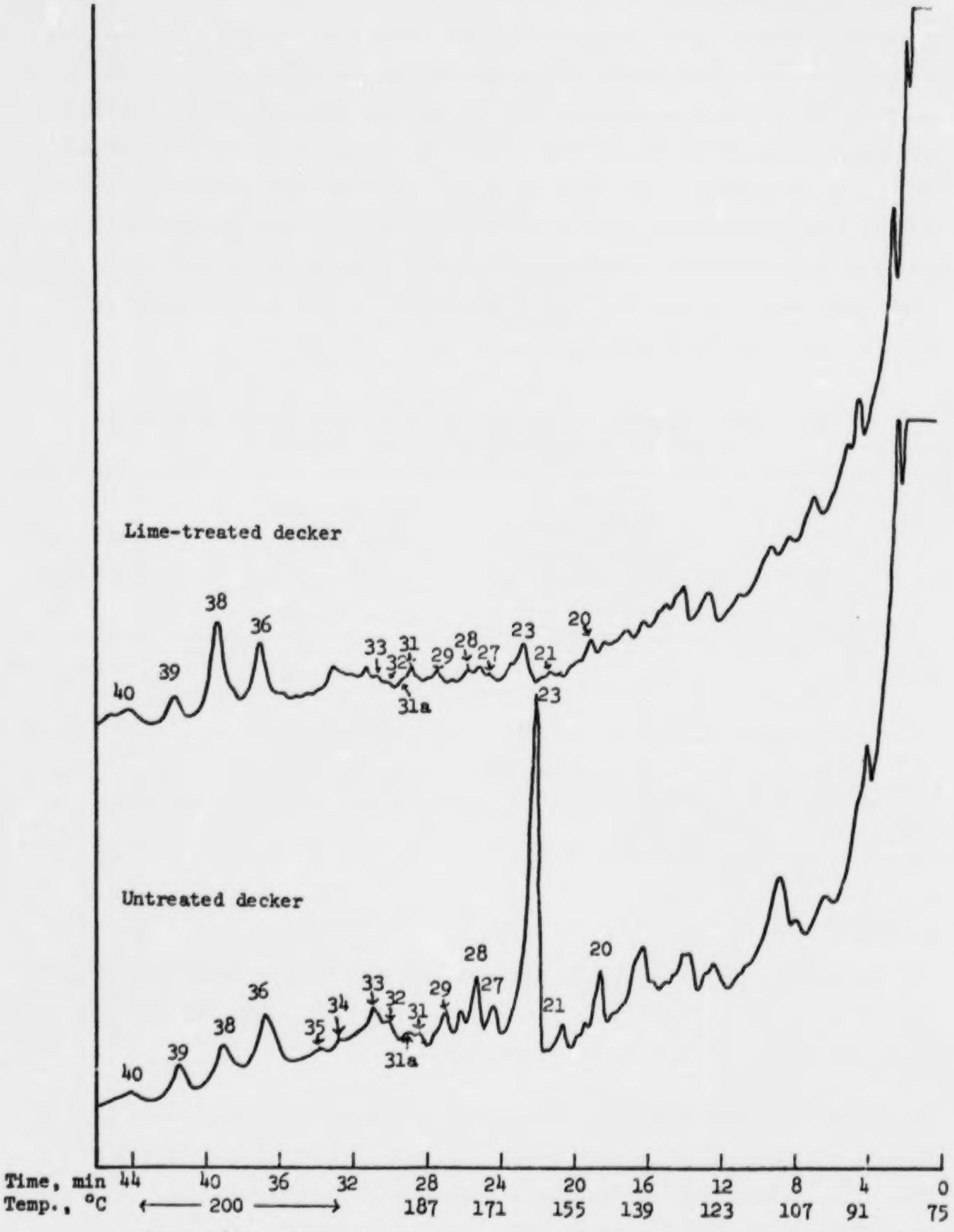

Figure 42. Pyrolysis gas chromatograms of untreated and lime-treated decker effluents from CONCO

that upon acidification 48.2 percent color and 36.0 percent TOC were recovered in the acid-insoluble fractions. The acid-soluble fraction contained more color (51.8 percent) and more TOC (64 percent) than the acid-insoluble. The lime-treated wastes on the other hand yielded 57.8 percent color (20.8 out of 36) and 51 percent TOC in the acid-insoluble fraction compared to 42 percent color (15.2 out of 36) and 49 percent TOC in the acid-soluble. This is different than the situation found in decker effluents where major portions of color in the untreated waste was found in the acid-insoluble component. Table 28 further shows that lime-treatment removes more color and TOC from the acid-soluble color bodies (70.6 and 46.4 percent).

Table 28. CHANGE IN SOLIDS ISOLATED FROM CONCO EFFLUENTS DUE TO STOICHIOMETRIC LIME TREATMENT

	Untreated NSSC waste		Lime-treated NSSC waste		Reduction due to lime	
Fractions	Color[a] yield, %	TOC[b] yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
NSSC waste	100	100	36	70	64	30
Acid-insoluble	48.2	36.0	20.8	35.7	56.8	<1.0
Acid-soluble	51.8	64.0	15.2	34.3	70.6	46.4

[a] APHA color, Pt-Co units.
[b] Total organic carbon.

Column Chromatography —

The acid-insoluble and acid-soluble color bodies were fractionated as before on Bio-Gel and XAD-8 columns, respectively. The results are given in Table 29 (for details see Appendix V).

The data show that Fraction "A" of the untreated acid-insoluble color bodies contains 32.4 percent color (15.6 out of 48.2) and 45 percent TOC. The lime-treated Fraction A contains 30.3 percent color (6.3 out of 20.8) and 27.0 percent TOC.

Table 29. FRACTIONATION OF NSSC ACID-INSOLUBLE COLOR BODIES BY COLUMN CHROMATOGRAPHY

	Untreated acid-insoluble color bodies		Lime-treated acid-insoluble color bodies		Reduction due to lime[c]	
Fractions	Color yield, %	TOC yield, %	Color yield, %	TOC yield, %	Color, %	TOC, %
Fraction "A" from P-2 column through P-60						
A_1	7.4	9.6	4.1	4.3	44.6	55.2
A_2	5.5	6.3	1.9	4.2	65.4	33.4
$A_3 + A_4$[a]	2.7	0.3	0.3	0.8	88.9	—
Acid-insoluble color bodies through P-2 column						
A	15.6	16.2	6.3	9.3	59.6	42.6
B through J[b]	32.6	19.8	14.5	26.4	55.5	--
Unfractionated acid-insoluble color bodies	48.2	36	20.8	35.7	56.8	<1.0

Percentages of yield are calculated on the basis of untreated original waste.

[a] Calculated by difference so that values for A = $(A_1 + A_2 + A_3 + A_4)$.

[b] Calculated by difference so that values for unfractionated acid-insoluble color bodies = (A + B through J).

[c] Values calculated from "yield" data of the solids isolated from untreated and lime-treated effluents.

The average color and TOC removed from acid-insoluble color bodies were 56.8 percent and < 1.0 percent, respectively (TOC removal figures are much lower than expected).

The acid-soluble color bodies were fractionated on XAD-8 resin and the data are given in Table 30. The results show that on the basis of untreated acid-soluble material Fractions III + IV combined contain 52.1 percent color (27 out of 51.8) and 47.5 percent TOC (30.2 out of 64), whereas on the basis of lime-treated material this combined fraction had 57.2 percent color and 29.5 percent TOC. The data further show that average color and TOC removed from acid-soluble color bodies were 70.6 and 46.4 percent, respectively. (These are based on actual determinations and not on mathematical averages from the data on fractions.)

Table 30. FRACTIONATION OF NSSC ACID-SOLUBLE COLOR BODIES BY COLUMN CHROMATOGRAPHY

Fractions	Untreated acid-soluble color bodies: Color yield, %	Untreated acid-soluble color bodies: TOC yield, %	Lime-treated acid-soluble color bodies: Color yield, %	Lime-treated acid-soluble color bodies: TOC yield, %	Reduction due to lime[a]: Color, %	Reduction due to lime[a]: TOC, %
IV	15.1	19.2	6.0	6.3	60.3	67.2
III	11.9	11.0	2.7	3.8	77.3	65.5
II	15.9	23.6	4.5	11.3	71.7	52.1
I	5.2	10.3	1.6	5.5	69.2	46.5
Unfractionated acid-soluble color bodies	51.8	64	15.2	34.3	70.6	46.4

Percentages of yield are calculated on the basis of untreated NSSC waste.

[a] Values calculated from "yield" data of the solids isolated from untreated and lime-treated effluents.

It can be concluded that in the case of untreated color bodies most of the color and TOC are obtained in the acid-soluble fractions, whereas in lime-treated samples it is the opposite. Lime removes more color and TOC from the acid-soluble color bodies.

Characterization of Effluent Fractions —

Individual fractions from chromatography columns were later combined to give larger acid-insoluble fractions "A" and C-J, and acid-soluble fractions I + II and III + IV.

Visible and UV Spectra —

Absorptivity values from the spectra at pH 7.6 were calculated as before and plotted in Figures 43-46. As no "lignin" such as "Indulin-C" for kraft, was available for NSSC effluent, the absorptivity values of Indulin-C were, therefore, used for comparison.

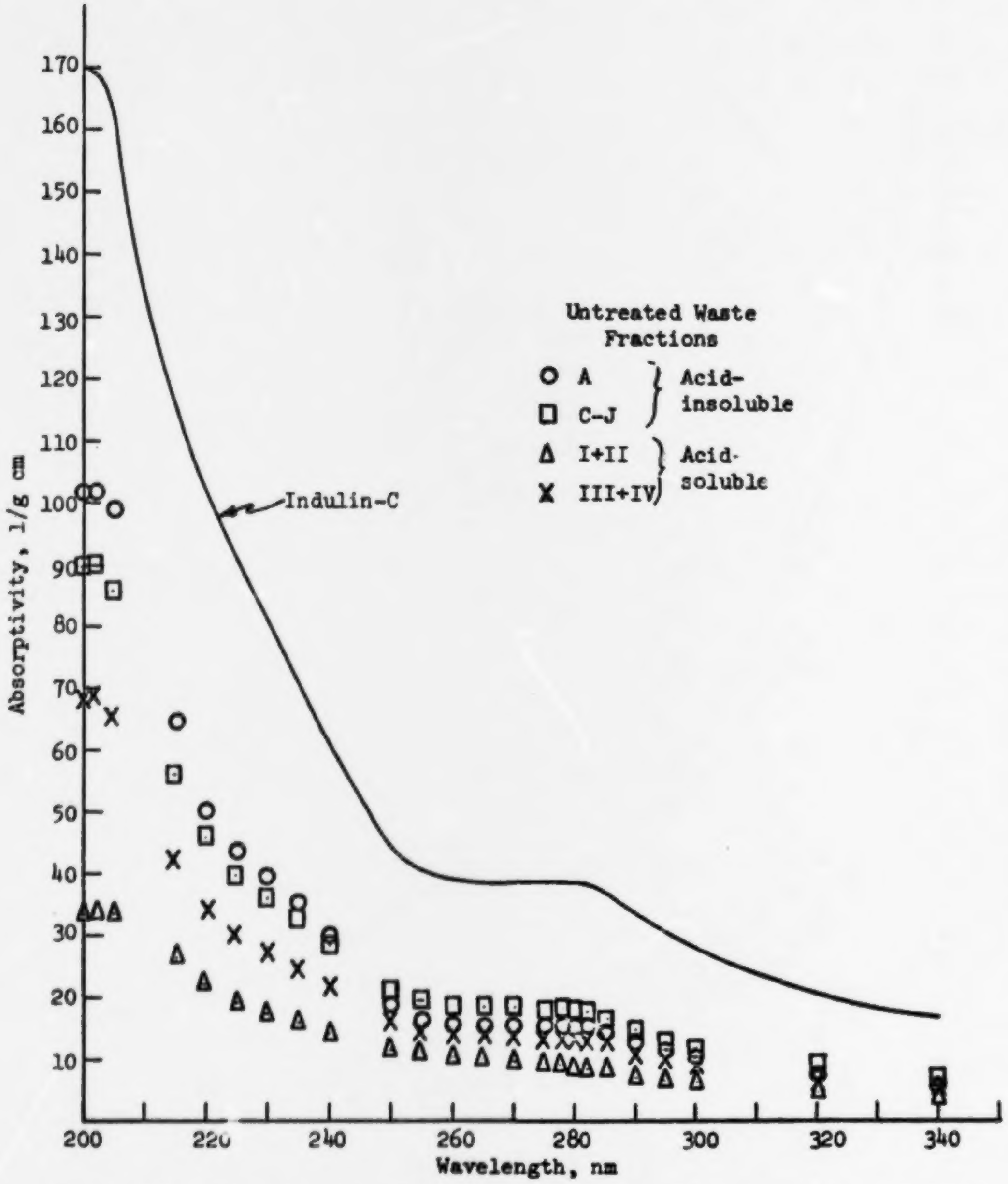

Figure 43. Absorptivity versus wavelength (ultraviolet range) of Indulin-C and untreated NSSC waste from CONCO

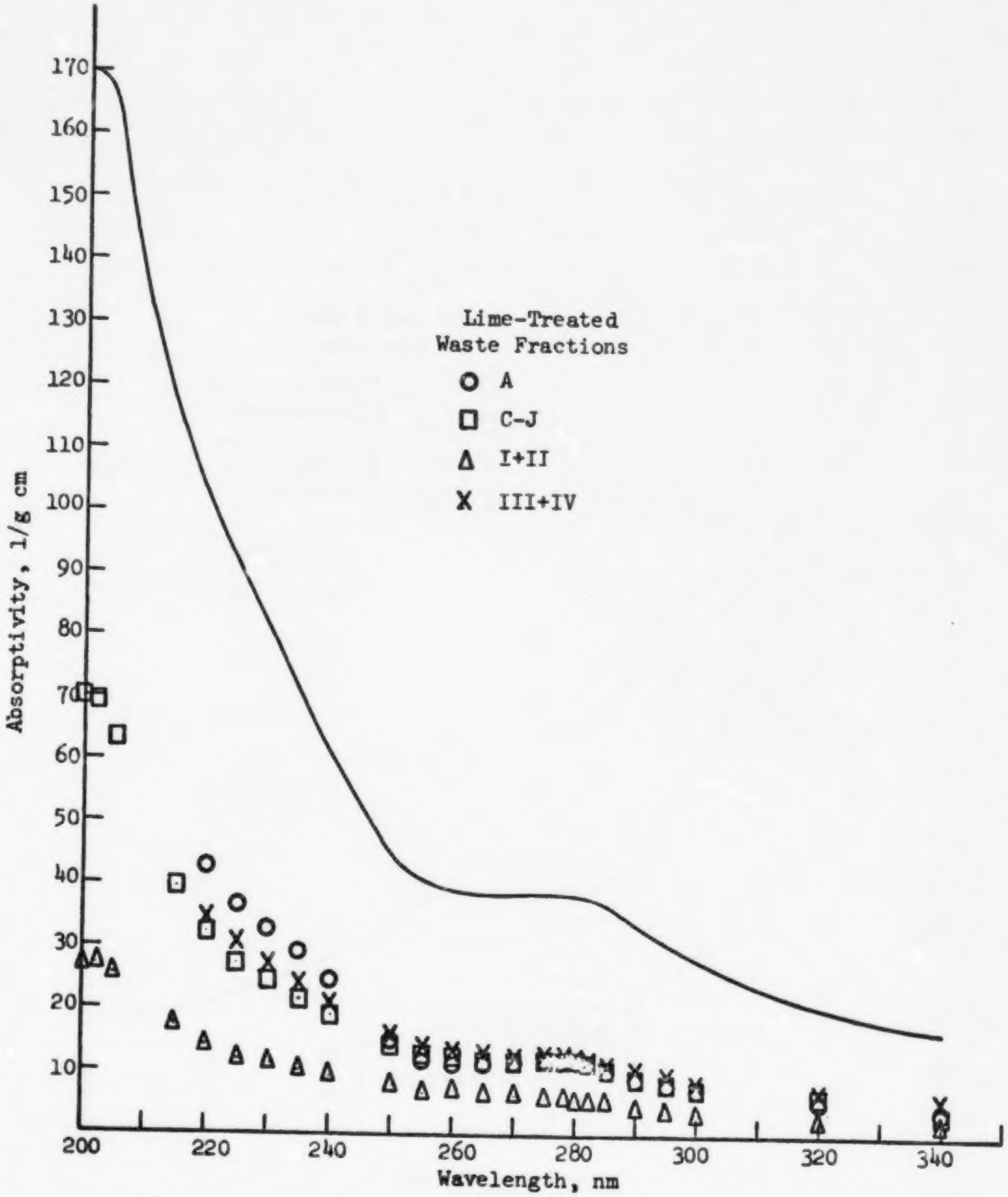

Figure 44. Absorptivity versus wavelength (ultraviolet range) of Indulin-C and lime-treated NSSC waste from CONCO

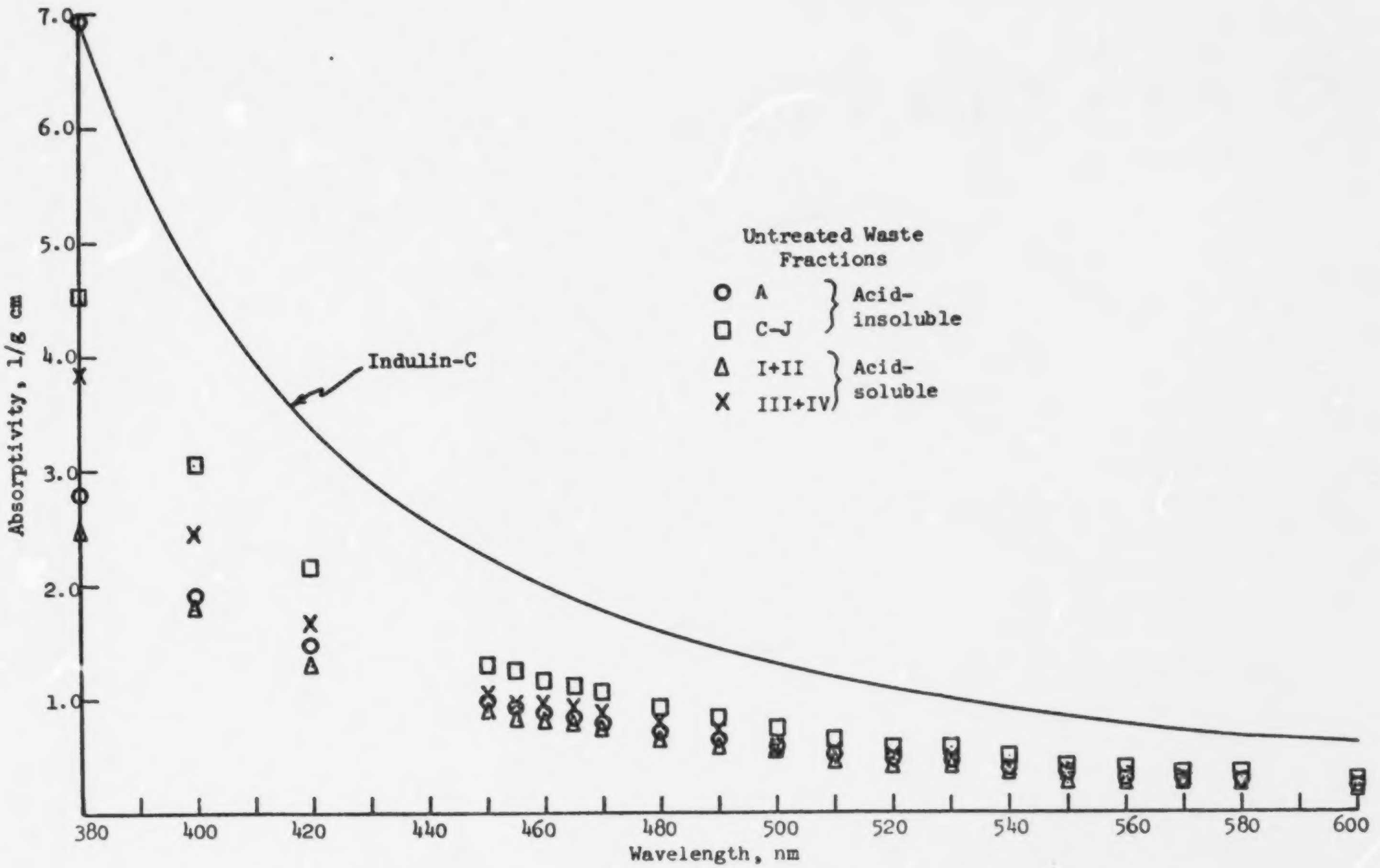

Figure 45. Absorptivity versus wavelength (visible region) of Indulin-C and untreated NSSC waste from CONCO

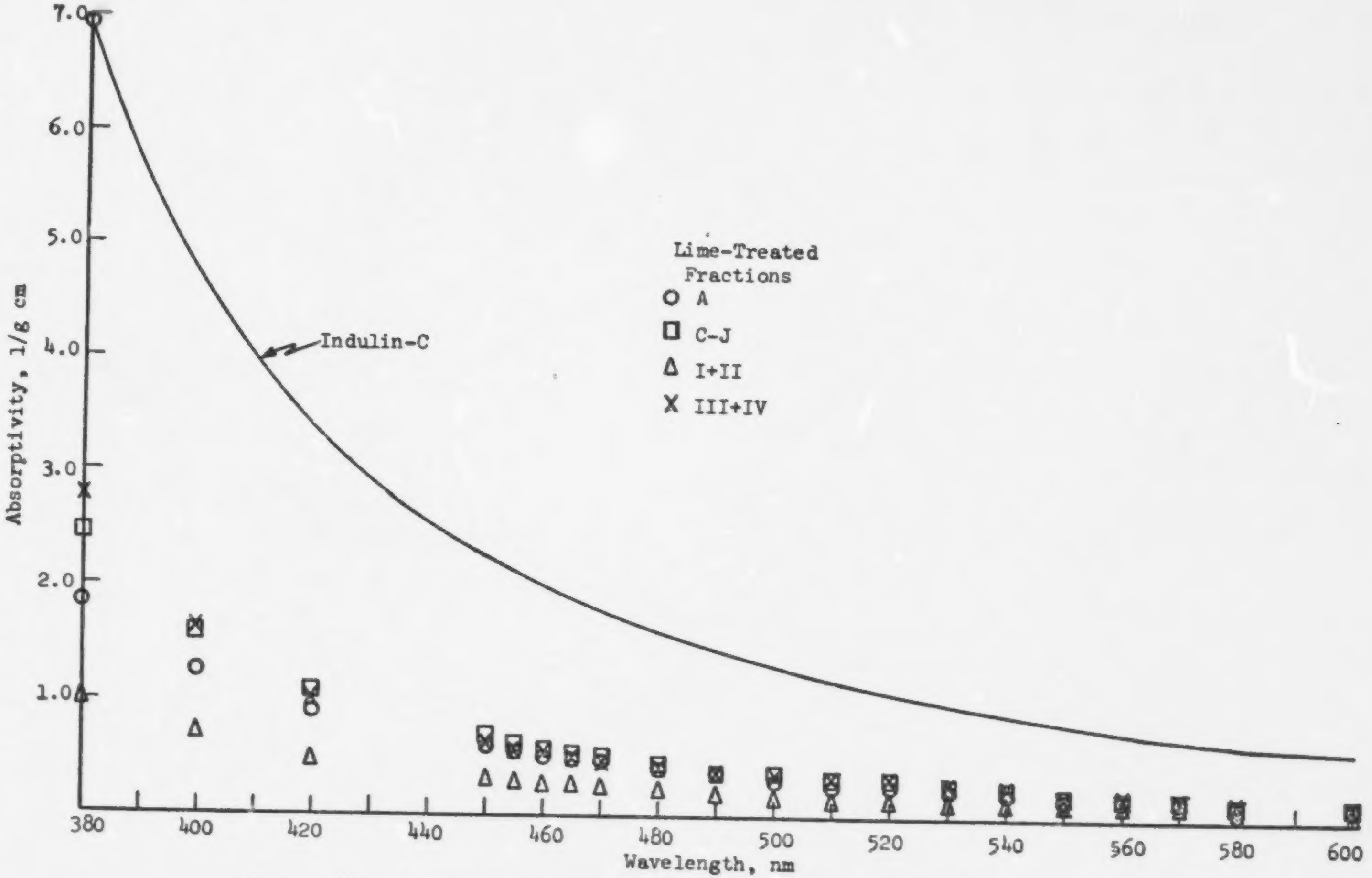

Figure 46. Absorptivity versus wavelength (visible region) of Indulin-C and lime-treated NSSC waste from CONCO

Ultraviolet region (Figures 43 and 44) — All samples exhibited an increase in absorptivity as the wavelength de-creased. The spectra also show "shoulders" at 280 and 205 nm. Generally, the untreated acid-soluble color bodies have lower absorptivity values than untreated acid-insoluble color bodies. This trend changes after lime treatment. Except acid-soluble Fractions III and IV, all other fractions showed a decrease in absorptivity after lime treatment. The values for Fraction III + IV did not change much after lime treatment. Indicating that either the color bodies from this fraction are not removed at all or, if they are, they are removed in the same ratio so that the absorptivity does not register any change. From previous data (Table 30) it is seen that about 46 percent TOC is in fact removed by lime.

Visible region (Figures 45 and 46) — All samples gave simple absorption curves and the absorptivities of all lime-treated fractions were lower than the untreated ones, indicating the removal of more color bodies. Surprisingly, the untreated acid-insoluble Fraction C-J and acid-soluble Fraction III + IV had higher absorptivity in the visible region than the untreated Fraction "A."

Molecular Weight Distribution —

Molecular weight ranges are plotted in Figures 47a and b. The results show that the weight average molecular weights of untreated acid-insolubles range from 600 to 40,000 and that of lime-treated acid-insolubles from 300-25,000. The acid-soluble color bodies before lime treatment range from 400-1200 and after lime treatment from 200-800.

The percentage removal data fluctuated so that definite relationships between percent removal and M_w could not be drawn. However, it was established that acid-insoluble color bodies having M_w of 300 were not removed by lime. There was a partial removal in M_w range of 300-25,000 and over 25,000 complete removal occurred. Data further showed that only a very small amount of material fell in the high M_w range.

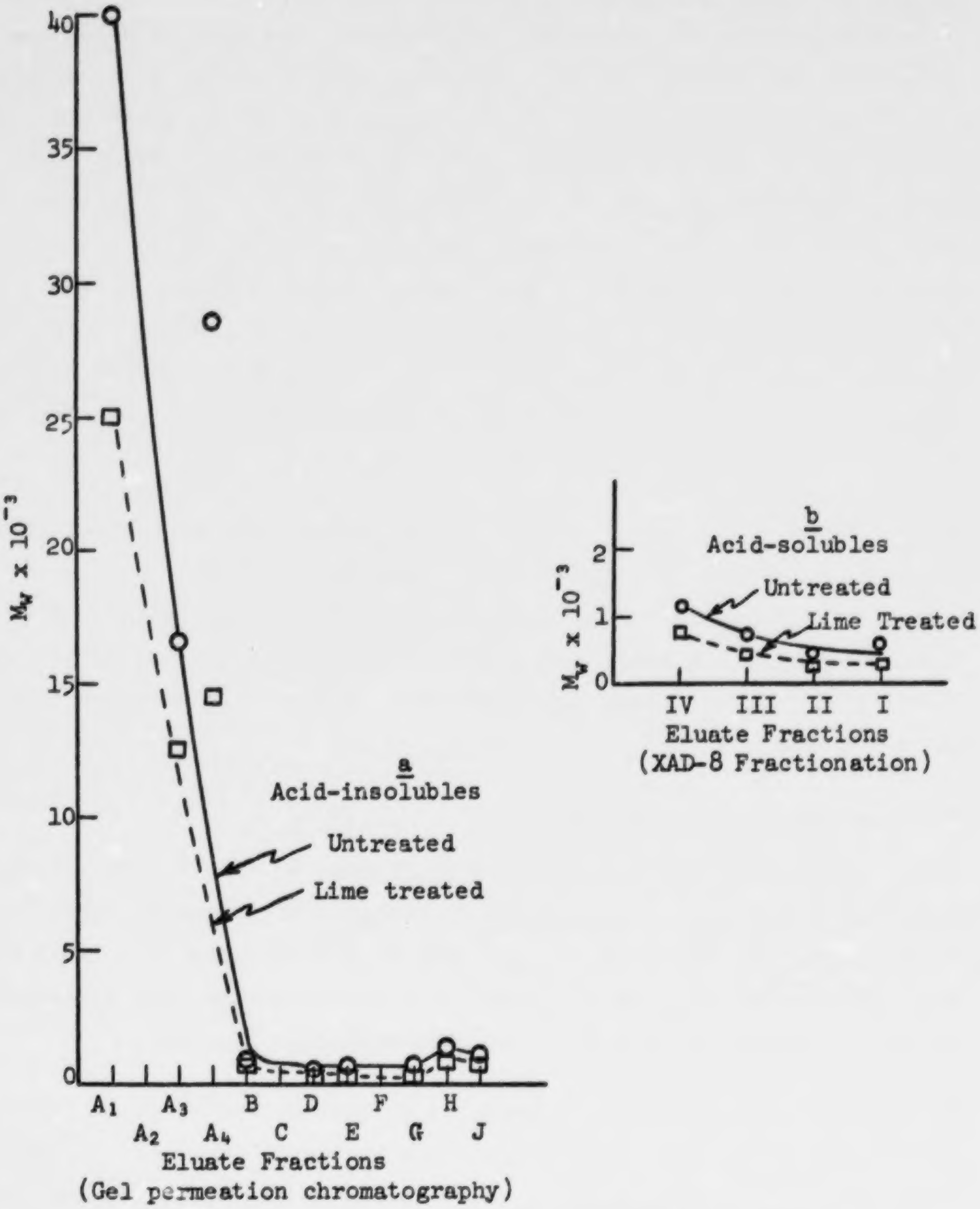

Figure 47. Weight average molecular weight (M_w) distribution of fractionated color bodies from NSSC effluent from CONCO (M_w at ω^2=0)

The acid-soluble color bodies behaved differently in NSSC effluent. In these color bodies, those above M_w of 770 were completely removed, below M_w 230 were not removed and partial removal occurred in the intermediate range of 230-770. Maximum M_w found in untreated acid-soluble color bodies was 1150. About 65 percent removal occurred at M_w of 720, so that between M_w 720 and 770 the percentage removal jumped from 65 to 100 percent.

Chemical Characterization –

The results of the chemical analysis are given in Table 31. The results show:

a. The meq phenolic hydroxyls per gram of volatile solids do not change appreciably during lime treatment. In all other effluents it was reduced.

b. The amount of total sugars per gram of volatile solids increases by about 62 percent after lime treatment, indicating that more of the non-sugar volatile solids compared to the sugars are removed.

c. Average methoxyl content in the unfractionated (original) waste decreases from 7.72 to 6.97 percent (9.7 percent reduction), indicating that the ratio of MeO to volatile solids remains almost unchanged by lime treatment. This, however, does not agree with the fact that sugars are not removed. Appreciable reduction in MeO occurs in Fraction "C-J" during lime treatment. It cannot be established whether this reduction is real or caused by preferential carbon fractionation in Bio-Gel columns.

d. Higher E_{420}/MeO ratio of untreated acid-soluble Fraction "I + II" indicates loss of MeO in this fraction. It is also substantiated by higher E_{280}/MeO, and E_{420}/E_{280} ratios indicating higher color compared to the aromatic nature.

e. E_{465}/E_{600} ratios indicate that all fractions have more open structures than Indulin-C.

Table 31. ANALYTICAL DATA ON FRACTIONS FROM NSSC EFFLUENT FROM CONCO
(Basis o.d. Solids)

	Indulin-C	Untreated NSSC					Lime-treated NSSC				
			Acid-insoluble		Acid-soluble			Acid-insoluble		Acid-soluble	
		Original	A	C-J	III + IV	I + II	Original	A	C-J	III + IV	I + II
Mol. wt. range	--										
Color recovery, %	--										
Ash[a], %	53.8	56.6	16.79	59.29	39.90	60.00	76.2	19.26	71.32	37.58	60.51
Volatile solids[b], %	46.20	43.4	83.21	40.71	60.10	40.00	23.8	80.74	28.68	62.42	39.49
Phenolic hydroxyls, meq/g	1.32	0.39	—	—	—	—	0.38	—	—	—	—
Total sugars[c], %	--	10.79	—	—	—	—	17.25	—	—	—	—
Methoxyl (MeO), %	21.05	7.72	14.60	11.22	8.88	4.13	6.97	15.33	7.71	9.01	3.24
E_{420}	3.9	1.37	1.47	2.14	1.68	1.32	0.51	0.901	1.08	1.03	0.476
E_{280}	38.4	11.66	15.69	17.89	13.45	8.7	7.54	11.92	11.46	12.84	5.98
E_{420}/MeO ratio	0.16	0.177	0.101	0.191	0.189	0.320	0.073	0.059	0.14	0.114	0.147
E_{280}/MeO ratio	1.82	1.51	1.07	1.59	1.51	2.11	1.08	0.778	1.49	1.43	1.85
E_{420}/E_{280} ratio	0.088	0.117	0.094	0.120	0.125	0.152	0.067	0.076	0.094	0.080	0.080
E_{465}/E_{600} ratio	3.14	3.02	3.61	4.44	4.43	4.15	4.0	3.58	3.89	4.66	3.62

[a] Ashed at 600°C, 1 hour and calculated on o.d. material.
[b] Volatile solids = 100-% ash.
[c] For individual sugars see Appendix IV.

E_{280}, E_{420}, E_{465}, and E_{600} are absorptivities at indicated wavelengths.

Infrared Spectra —

The IR spectra for this series do not reveal significant differences in the organic material that could be attributed to lime treatment. Sulfate and, in the case of lime-treated samples, carbonate are the most obvious inorganic components present. Sulfite does not seem to be present, but it is not possible to rule out small amounts of thiosulfate. This series is distinguished from the others by bands suggesting the presence of lignosulfonates in small amounts.

The region 1400-1650 cm^{-1} is particularly interesting in distinguishing differences between acid-insoluble and acid-soluble material. The ratio of intensities of carboxylate bands to aromatic ring bands in this region is much higher for the acid-soluble materials than for the acid-insoluble materials. The acid-soluble fractions thus seem to have a much higher carboxylate content and this increased polarity is undoubtedly a major factor in determining solubility.

Untreated NSSC waste (Figure 48) — The intensity of the broad band at 3400 cm^{-1} agrees with the high water content of this sample. Sulfate is evident as a major component of the ash, giving bands at 1140 and 620. There is no sign of sodium sulfite in this spectrum or in any of the spectra of fractions. A weak band at 995 may be indicative of thiosulfate. The carboxylate bands are quite intense at 1575 and 1410. Lignin is probably responsible for the band at 1040 and shoulders at 1460 and 1510.

The region between 1400 and 1600 is quite interesting in this series. The appearance of absorption is thought to reflect the relative amounts of carboxylate salt groups and aromatic nuclei present. In this sample the carboxylate salt groups are quite dominant, and their broad bands overlap the aromatic bands of the lignin so that the latter appear only as shoulders. The relative amounts of these groups change dramatically during fractionation as will be pointed out in the ensuing discussion. One other distinctive feature of the spectrum is the shoulder at 655 and weak broad band at 530. This is attributed to lignosulfonate, which is a reasonable component for this particular effluent.

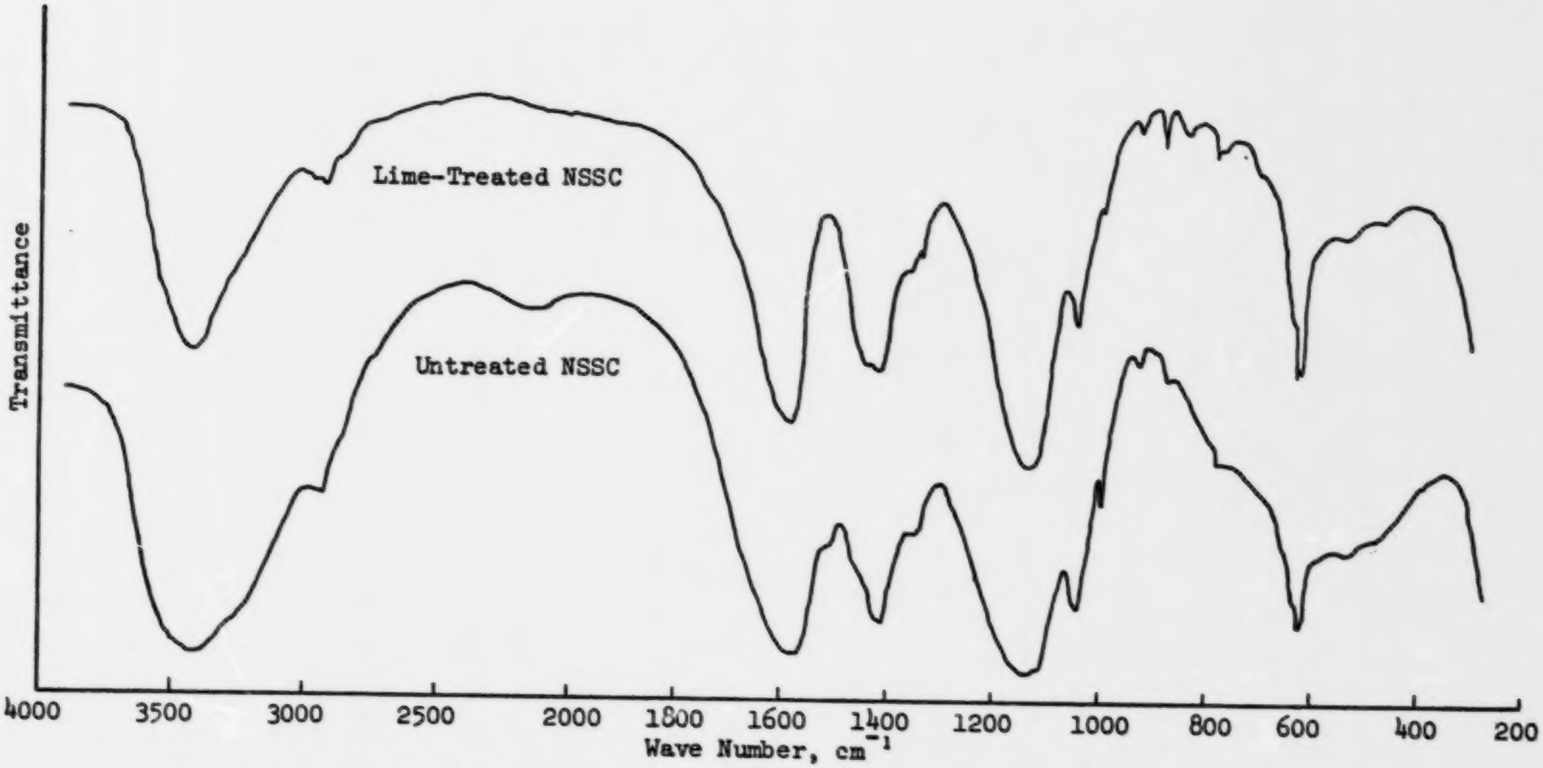

Figure 48. Infrared spectra of untreated and lime-treated color bodies from NSSC effluent from CONCO

Lime-treated NSSC waste (Figure 48) — The general appearance of the spectrum is very similar to that of the untreated sample. The lignin bands are less evident in the lime-treated sample at 1500 and 1040 cm^{-1}.

The sulfate bands are comparable to those in the spectrum of the untreated sample. The presence of carbonate is suggested by the broadening of the band at 1410 in the untreated sample to a wide maximum (1410-1450) in the lime-treated sample. Further evidence for carbonate is the sharp peak at 875 cm^{-1}, which is also noted in other lime-treated samples in other series. Evidence for a small amount of lignosulfonate is also present in this spectrum.

The disappearance of the lignin band at 1510 cm^{-1} does not necessarily signify a marked structural change in the lignin systems resulting from action of lime. This lignin band could have been simply obscured by the combined influence of neighboring carboxylate and carbonate bands.

Untreated acid-insoluble Fraction "A" (Figure 49) — This fraction is comparatively low in ash and the sulfate content is clearly much lower than is the case for the original effluent sample (judging from the absorption at 1130 and lack of absorption at 620). The lignin-related bands at 1030 and 1500 are quite intense as would be expected from the high methoxyl content of 14.6 percent. A band at 1460 is also quite prominent and this, too, may be largely representative of the aromatic systems in lignin.

Careful comparison of the 1400-1650 for this fraction (Figure 49) and for untreated NSSC waste (Figure 48) suggests that the relative amounts of lignin (aromatic systems) and carboxylate salts are very different in the two samples. Although it is not possible to make even semiquantitative statements, it appears that this region is dominated by lignin-related bands for the acid-insoluble fractions (though to a lesser extent for untreated acid-insoluble Fraction "C-J," whereas it is dominated by carboxylate salt bands for the acid-soluble fractions and the untreated NSSC waste.

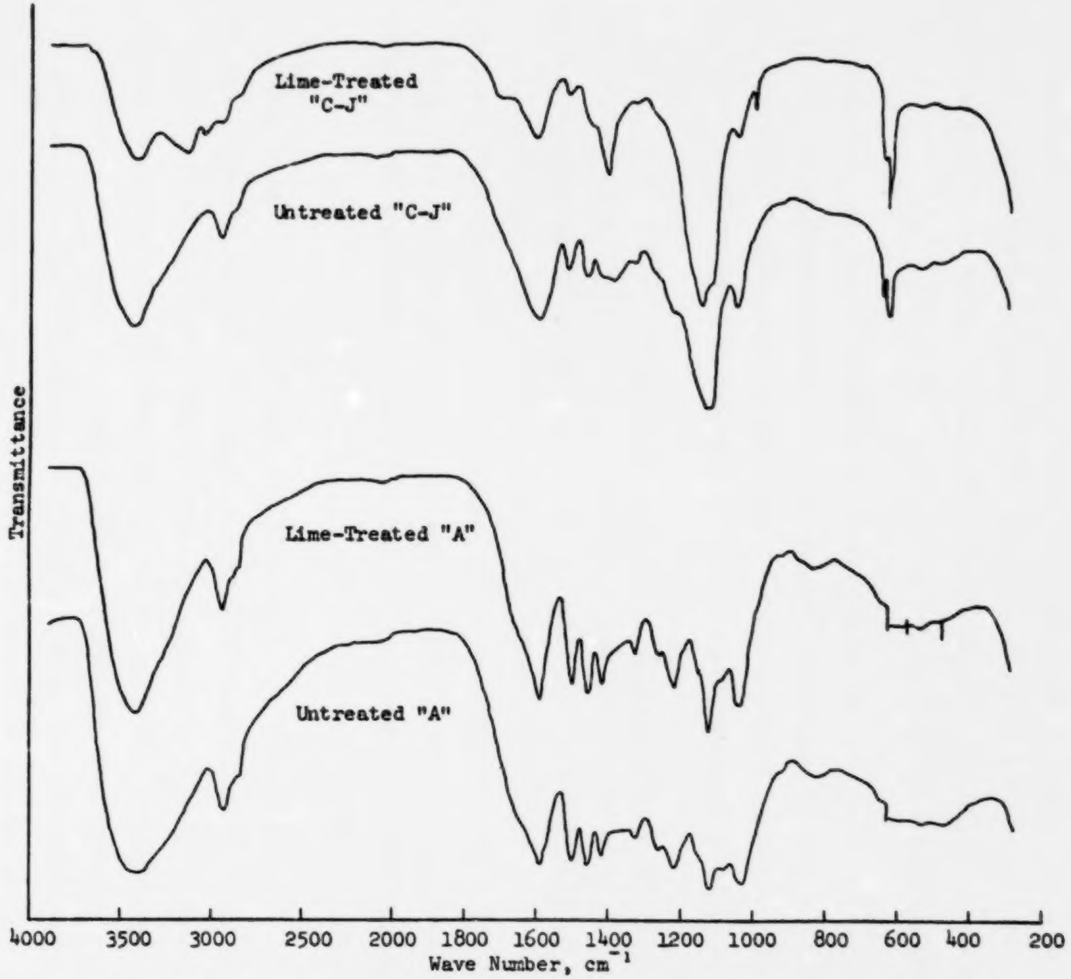

Figure 49. Infrared spectra of untreated and lime-treated acid-insoluble fractions from NSSC effluent from CONCO

Thus, the distinctive feature of the acid-insoluble fractions seems to be the relatively high ratio of lignin (or aromatic rings) to carboxylate systems. The lower polarity implied by this analysis would be expected to result in lower water (or acid) solubility, as is indeed the case.

Lime-treated acid-insoluble Fraction "A" (Figure 49) — This sample appears extremely similar to its untreated counterpart. The ash content, methoxyl content, and the IR spectra show few differences. The ratio of lignin bands to carboxylate bands in the 1400-1650 region is almost identical in the two spectra. There are no differences significant enough to be interpreted as results of the lime treatment.

Untreated acid-insoluble Fraction "C-J" (Figure 49) — There is a high ash content (59.29 percent) and a substantial part of it is sulfate, since there is a broad maximum at 1120 and related absorption at 620. This is a distinct difference relative to the untreated Fraction "A." Although bands at 1505 and 1030 and a methoxyl content of 11.22 percent suggest a considerable amount of lignin, this fraction is much richer in carboxylate salt content than untreated "A." This is deduced from the relative band intensities in the 1400-1650 region.

Lime-treated acid-insoluble Fraction "C-J" (Figure 49) — In comparing the spectrum of this fraction with its untreated counterpart, again there is little difference that could be attributed to the lime treatment. In the region 2900-3200 there are new bands apparent, and the band at 1400 is sharper and more intense than it usually is. This, however, is thought to be due to production of an artifact-ammonium ion during the column fractionation. This is even more clearly revealed in the untreated "C-H" (see Figure 26), which was obtained at the same fractionation stage but came from a caustic extract effluent.

Acid-Soluble Material —

Untreated acid-soluble Fraction "I + II" (Figure 50) — This sample is characterized by high ash (60.00 percent) and the lowest methoxyl content

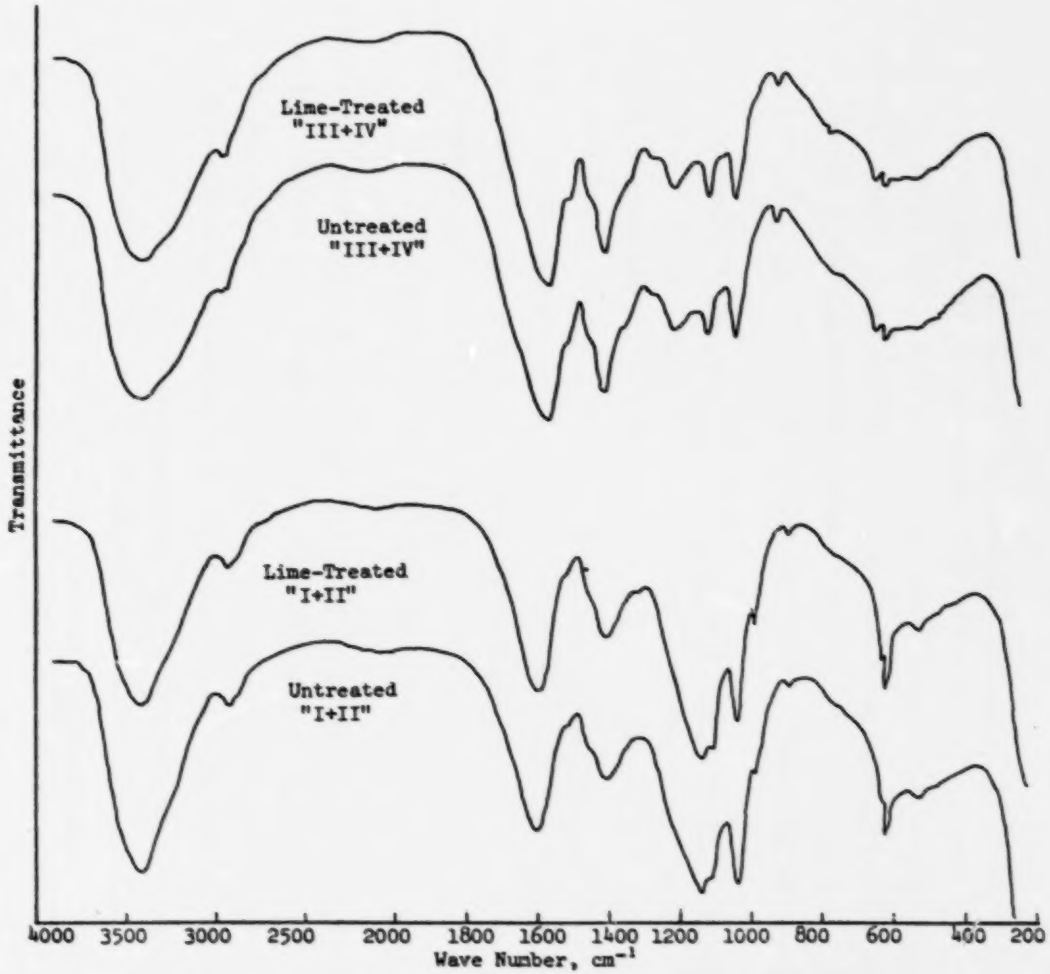

Figure 50. Infrared spectra of untreated and lime-treated acid-soluble color bodies from NSSC effluent from CONCO

(4.13 percent) of any of the five untreated NSSC waste fractions (the original NSSC effluent sample and the four fractions derived from it).

A substantial component of the inorganic material appears to be sulfate, as seen by strong bands at 1140 and 625. A probable lignin-related band is quite prominent at 1040. The region between 1400 and 1650 is dominated by the carboxylate salt bands at 1410 and 1605. The lignin-related bands at 1500 and about 1460 are seen in this spectrum only as shoulders.

The general appearance of this region, and even the entire spectrum, is very similar to that seen for the untreated NSSC waste sample. The primary difference between the organic material in this fraction and the organic material present in the acid-insoluble fractions is that the ratio of carboxylate groups to lignin-related ring systems is much greater for the acid-soluble sample. The suspected lignosulfonate band at 530 is most prominent in the spectrum of this acid-soluble material.

Lime-treated acid-soluble Fraction "I + II" (Figure 50) — This lime-treated fraction has ash (60.51 percent) and methoxyl content (3.24 percent) comparable with its untreated counterpart discussed above. The IR spectra of these fractions are virtually identical and the effect of lime treatment is not at all apparent from the IR spectra.

Untreated acid-soluble Fraction "III + IV" (Figure 50) — This sample contains lower ash (39.90 percent) and higher methoxyl (8.88 percent) than the other acid-soluble fraction just discussed. The spectrum suggests that lignin content is indeed higher since prominent bands are present at 1045 and 1210. Sulfate may be contributing to the absorption at 1120 and 625. Weak bands whose origin is uncertain, are seen at 925 and 650. The 925 band is also evident in the untreated NSSC sample, but the 650 band would be masked by sulfate absorption.

The region between 1400 and 1650 is quite similar to that of the other acid-soluble fraction ("I + II"), suggesting that both acid-soluble fractions contain organic material that has a relatively high ratio of carboxylate to lignin-related ring systems. This ratio appears similar to that of the original untreated sample but is clearly much higher than is the case for the acid-insoluble fractions.

The primary difference between the two acid-soluble fractions seems to be that of inorganic content. Molecular weight differences may also exist but could not be detected from the IR spectra.

Lime-treated acid-soluble Fraction "III + IV" (Figure 50) — Again there is no significant difference in ash content, methoxyl content, or IR spectra between this fraction and its untreated counterpart.

Pyrolysis Gas Liquid Chromatography —

Qualitative pyrolysis GLC was run on untreated and lime-treated NSSC effluent from CONCO. The chromatograms are given in Figure 51. Both chromatograms are quite similar. The color bodies in NSSC waste contain some of the compounds obtained by pyrolyzing Indulin-C. Note the peaks marked 21 to 32. These have been previously identified (see Figure 18 and Table 13).

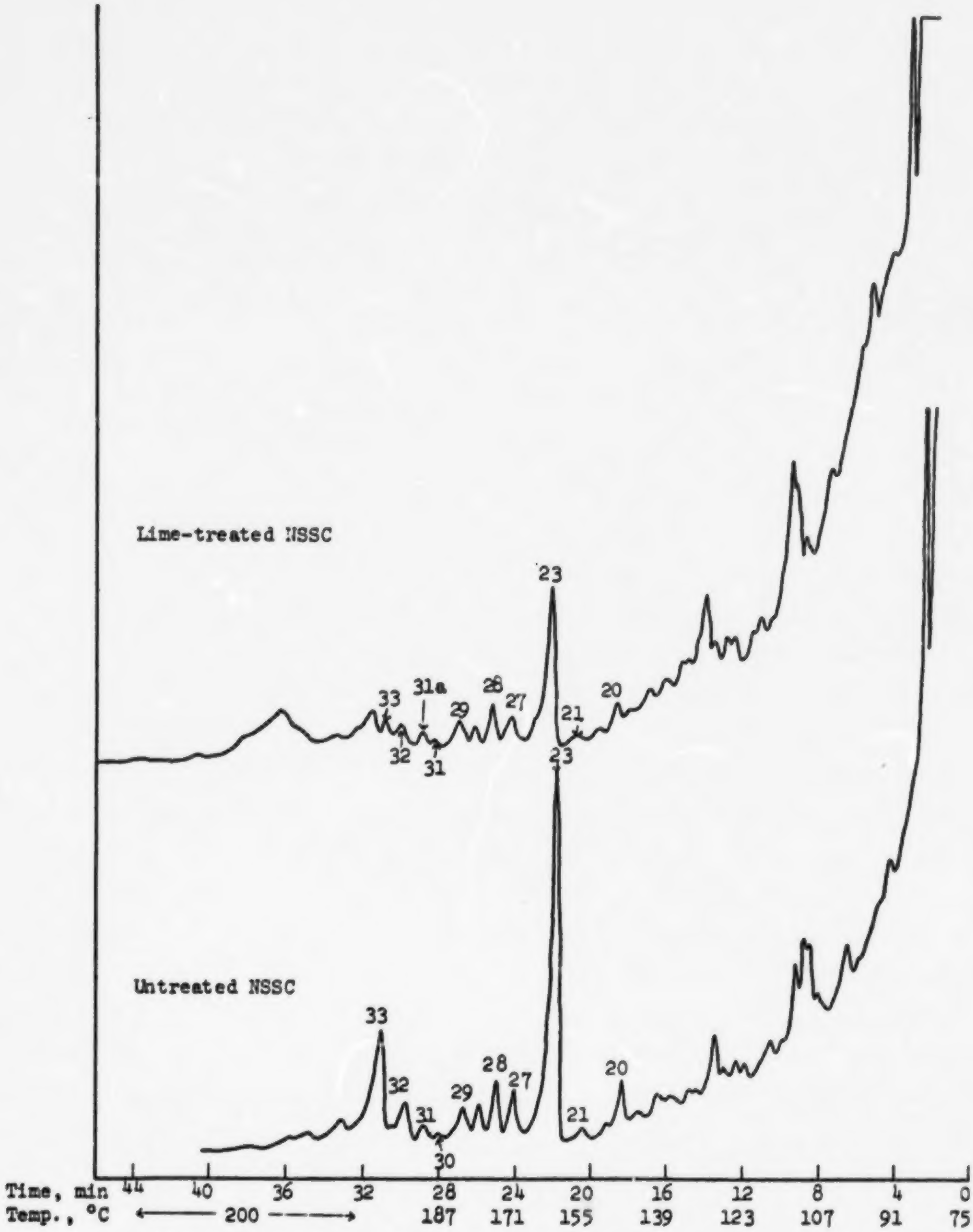

Figure 51. Pyrolysis gas chromatograms of untreated and lime-treated NSSC effluents from CONCO

SECTION VI

LIME TREATMENT WITH METAL IONS

It was mentioned in the Introduction of this report that the objective of this phase of our study was to establish an improved lime treatment system for the removal of color from kraft decker effluents, kraft bleach caustic extract and NSSC effluents.

BACKGROUND INFORMATION

James, in his book entitled "Water Treatment" (Technical Press Ltd., 1965, p. 110-14), mentions that sufficient lime is added to water to combine with the free carbon dioxide and then to convert the bicarbonates of calcium and magnesium into carbonate and hydroxide, respectively. He further indicates the use of iron salts in clarification and subsequent addition of alkali to precipitate the iron. Small amounts of lime have also been used to produce "ferric flocs."

Although the use of lime as a water softener is quite old, its use as a color flocculant in kraft industry is fairly recent. Lime precipitation has been shown to remove certain solid constituents and 85 to 90 percent of color from the kraft pulping waste. Excessive amounts of lime (over the minimum required) have no apparent effect on percentage of color removal. Preliminary studies at the Institute have shown that, by the addition of certain multivalent ions with lime, practically all of the color is removed.

The objective of this work was to establish conditions for such an "improved lime-treatment system." This study was divided into 3 major steps:

1. Treatment of mill wastes with metal ions.
2. Treatment of mill wastes with varying metal ion concentration and constant lime concentration.
3. Treatment of mill wastes with varying lime concentration and constant metal ion concentration.

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TREATMENT OF MILL WASTES WITH METAL IONS

Preliminary color removal studies were performed on untreated kraft wastes from the decker and the caustic extraction stages using salts such as alum, barium chloride, ferric chloride, magnesium hydroxide and zinc chloride.

Concentrated salt solutions (6000 ppm) were individually prepared and stored for future use. Freeze-dried color bodies from decker and caustic extraction stages were dissolved in distilled water to give 0.1 percent solutions which, eventually, were used for this study.

The desired amount of salt solution to give 100-1000 ppm salt per 50 ml total volume was measured into graduated cylinders and filled to the 50-ml mark with the waste to be evaluated. Mixing was accomplished by inverting the graduates five times. The treated effluent was then allowed to stand undisturbed for a minimum of 15 minutes prior to centrifuging to remove flocculated material. Each treated sample was centrifuged for 15 minutes at 9000 rpm. The clear supernatant was carefully poured off and stored until tested for pH, color, absorbance, and total organic carbon (TOC). Only the ferric chloride treatment was run in two series. In one the pH was not adjusted and in the other pH was adjusted to about 9.0 with NaOH to produce "ferric floc" and then centrifuged. The sediment was discarded.

The percentage of removal of color and TOC were calculated from the data obtained (absorbance values at 280 nm were not very reliable because of interference by ferric ion) and the results are given in Tables 32 and 33. Only the color removal values are plotted against salt concentration in moles/liter in Figures 52 through 55.

A comparison of Figures 52 and 53 shows that $BaCl_2$ is a better color removing agent for decker effluent than for caustic extract. At the concentrations studied $Mg(OH)_2$ was the least effective.

Figures 54 and 55 show that alum is more effective in the case of decker effluent than caustic extract, whereas $FeCl_3$ is more effective on caustic

Table 32. TREATMENT OF KRAFT EFFLUENTS WITH BIVALENT IONS

Salt concentration		Decker effluent			Caustic extract		
ppm	10^{-4} moles/l	Final pH	Color removal, %	TOC removal, %	Final pH	Color removal, %	TOC removal, %
$Mg(OH)_2$							
0	--	7.2	--	--	8.2	--	--
100	17.15	7.4	0	3.3	8.4	0	1.6
200	34.3	7.5	2.5	3.5	8.7	6.8	4.5
250	42.9	7.8	2.5	6.2	8.9	11.4	5.7
300	51.5	8.0	5.0	3.9	9.0	11.4	8.0
350	60.0	8.0	2.5	5.9	9.0	11.4	4.5
400	68.6	8.1	7.5	11.3	9.1	12.0	7.4
600	103.0	8.0	7.5	15.4	9.2	22.8	13.2
$ZnCl_2$							
0	--	7.2	--	--	8.1	--	--
100	7.34	6.9	2.5	5.3	6.9	0	2.8
200	14.68	6.5	5.0	8.9	6.7	3.9	7.4
250	18.33	6.5	7.5	13.3	6.7	3.9	8.4
300	22.0	6.4	12.5	13.6	6.7	13.6	11.1
350	25.7	6.3	17.5[a]	13.9	6.7	13.4	14.3
400	29.33	6.2	22.5	17.7	6.7	22.9	21.3
600	44.0	6.0	45.4	40.8	6.7	44.0	46.5
$BaCl_2$							
0	--	7.2	--	--	7.1	--	--
100	4.8	7.3	5.0	6.5	6.9	0	6.0
200	9.6	7.2	16.7	8.3	6.5	0	4.3
250	12.0	7.1	21.7	9.5	6.5	0	6.3
300	14.4	7.0	23.3	10.1	6.6	+1.3	6.6
350	16.8	6.9	26.7	13.3	6.8	4.1	9.8
400	19.2	6.7	28.3	13.6	6.9	1.1	9.8
600	28.8	6.4	41.2	24.3	7.0	23.7	20.0
800	38.4	6.2	42.5	31.4	7.1	35.9	33.1
1000	48.0	5.7	61.2	40.8	7.1	45.2	42.9
$Ca(OH)_2$							
0	--	--	--	--	8.6	--	--
100	13.5	--	--	--	10.3	20.0	--
200	27.0	--	--	--	11.3	22.5	--
250	33.8	--	--	--	11.6	22.5	--
300	40.5	--	--	--	11.7	25.0	--
350	47.3	--	--	--	11.8	32.5	--
400	54.0	--	--	--	11.9	62.5	--
600	81.0	--	--	--	12.1	72.5	--

[a] Calculated value.

Table 33. TREATMENT OF KRAFT EFFLUENTS WITH TRIVALENT IONS

Salt concentration		Decker effluent			Caustic extract		
ppm	10^{-4} moles/l	Final pH	Color removal, %	TOC removal, %	Final pH	Color removal, %	TOC removal, %
Alum ($Al_2(SO_4)_3 \cdot 18H_2O$)							
0	--	7.2	--	--	7.9	--	--
100	1.42	7.3	59.1	23.9	6.5	7.7	22.1
200	2.84	5.1	87.1	--	4.8	63.1	64.5
250	3.55	4.7	90.9	--	4.4	85.2	74.1
300	4.26	4.6	88.1	--	4.3	84.6	71.9
350	4.97	4.5	88.2	58.0	4.2	85.2	72.1
400	5.68	4.5	88.2	52.8	4.3	84.6	75.8
600	8.51	4.5	86.8	54.2	4.1	86.5	75.7
$FeCl_3$ — pH unadjusted							
0	--	7.2	--	--	6.7	--	--
100	6.2	5.8	27.3	22.0	6.1	0	5.8
200	12.4	5.0	75.5	54.8	5.6	24.4	22.6
250	15.45	4.1	76.4	66.6	5.1	26.9	27.5
300	18.5	3.8	77.3	66.9	4.8	51.3	46.8
350	21.6	3.7	77.3	59.8	4.4	74.8	64.6
400	24.7	3.4	75.5	65.3	4.1	91.7	80.1
600	37.0	3.1	76.4	68.1	3.8	90.7	82.9
$FeCl_3$ — pH adjusted							
0	--	7.2	--	--	6.7	--	--
100	6.2	8.2	0	19.3	8.4	0.6	17.2
200	12.4	8.7	21.1	58.9	8.9	67.4	73.6
250	15.45	8.3	12.6	67.1	8.7	83.1	86.1
300	18.5	8.5	38.9	70.3	9.1	97.2	86.3
350	21.6	8.9	58.3	65.6	8.6	97.3	62.0
400	24.7	8.9	50.9	69.9	8.1	97.3	76.6
600	37.0	8.8	72.5	71.2	7.8	97.4	81.3

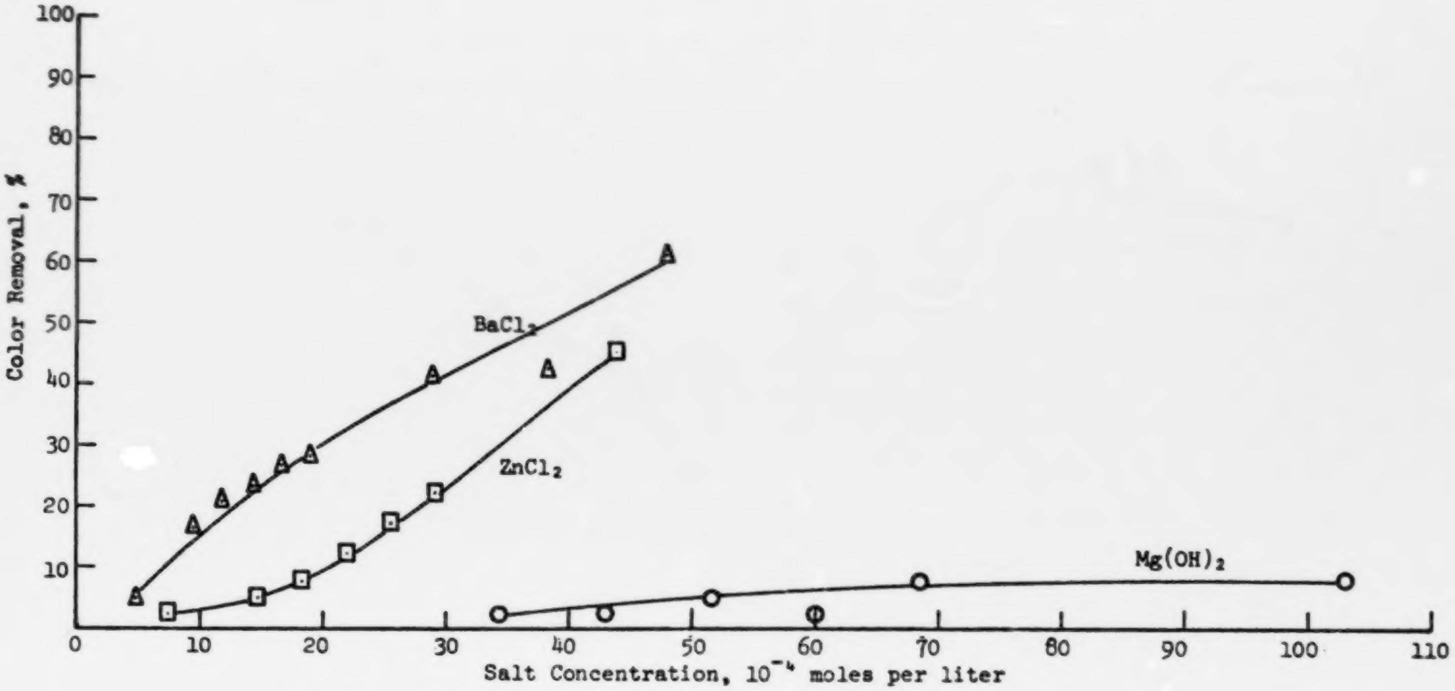

Figure 52. Treatment of kraft decker wastes with bivalent ions

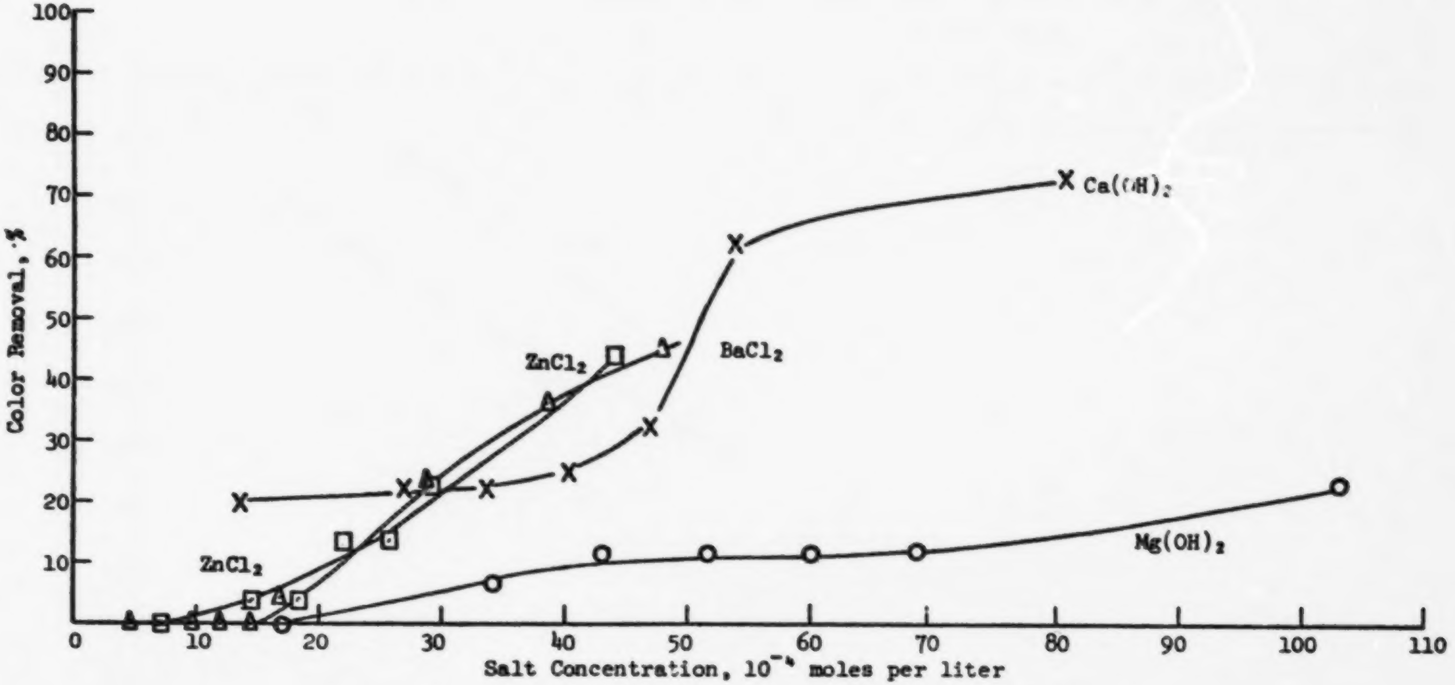

Figure 53. Treatment of kraft caustic extract with bivalent ions

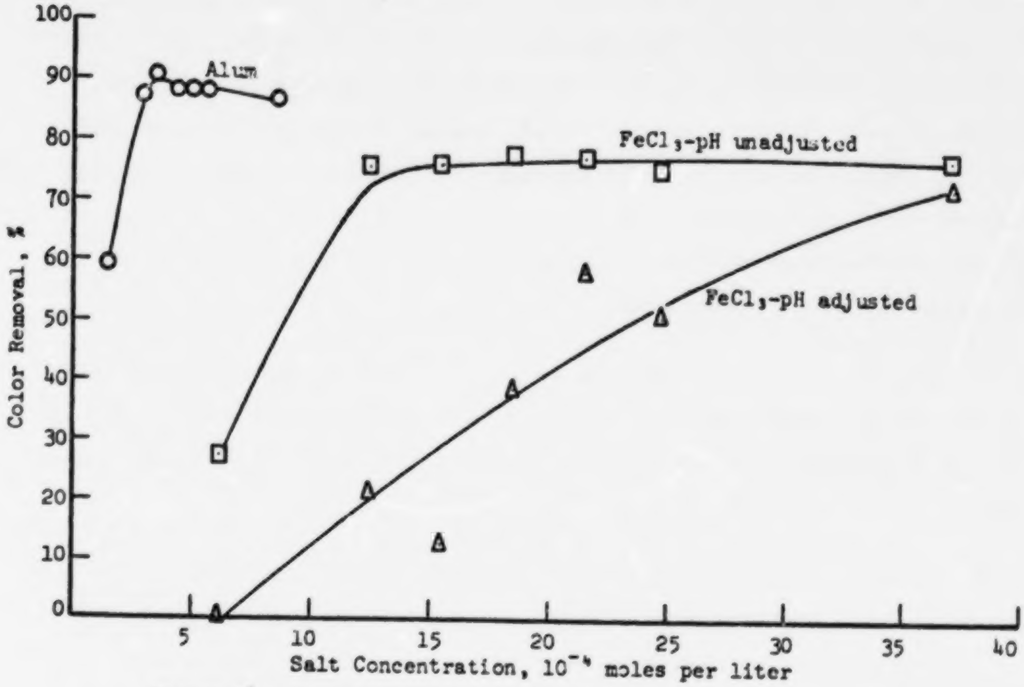

Figure 54. Treatment of kraft decker waste with trivalent ions

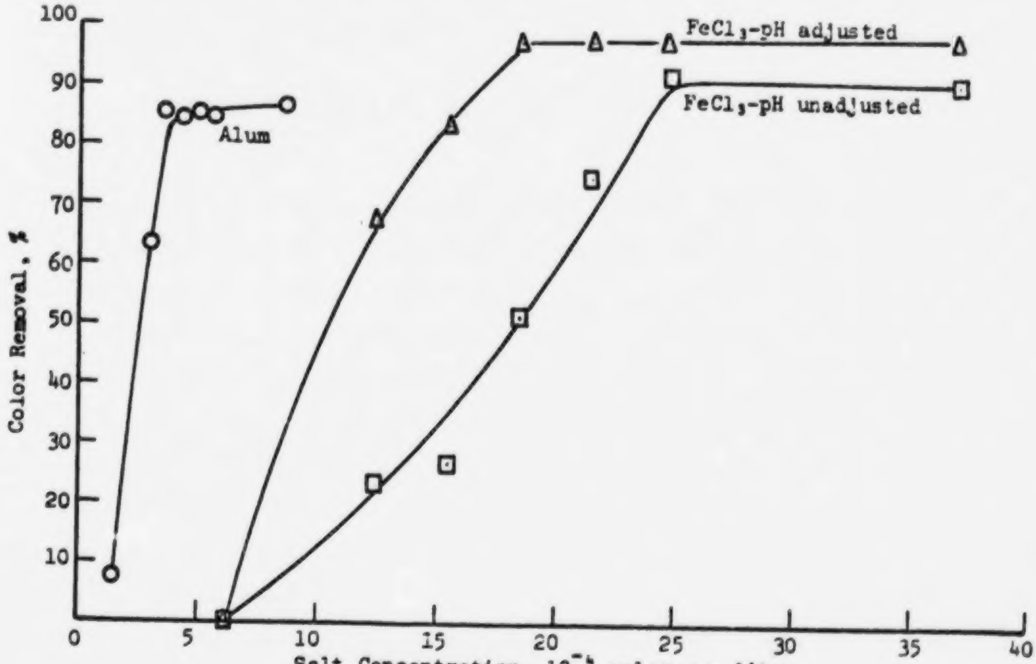

Figure 55. Treatment of kraft caustic extract with trivalent ions

extract. An interesting observation is that $FeCl_3$ removes more color from decker when the pH is not adjusted and is on the acid side. This situation reverses itself in the case of caustic extract. It seems that some decker color is precipitated because of lower pH and is removed with color-Fe complex. In the case of caustic, however, because of higher carboxyl content (see IR investigation, this report) less color is precipitated at lower pH but is taken out with the "ferric floc" under alkaline conditions.

The results, in general, show that trivalent ions are more effective color removing agents than the bivalent ions and that higher percentage of color is removed from caustic extract with $FeCl_3$ under alkaline conditions.

From the above results "optimum" levels of salt concentrations were found or in some cases projected over which no significant increase in color removal was achieved or expected.

Further experiments with metal ions and lime were planned in which metal compounds were varied below the established "optimum" addition levels.

TREATMENT OF MILL WASTES WITH VARYING METAL-ION CONCENTRATION AND CONSTANT LIME CONCENTRATION

Barium chloride and ferric chloride were the two salts used (in conjunction with lime) in the lime treatment of untreated and lime-treated caustic extract and NSSC effluents. Lime-treated effluents contained color bodies not removed by the conventional one-step lime-treatment process. The effluents were used in this study to find out whether or not more color can be removed by the metal ion-lime system. Lime concentrations for these runs were kept at 850-1000 ppm and the metal ions (as salts) were varied between 25-1500 ppm (ppm unit was used for easy understanding, conversion units are given for moles/liter wherever necessary). Freeze-dried color bodies from the effluents were dissolved in distilled water to give 0.2 percent solutions, which were then used for this study.

Forty milliliters of the above solution were measured into a 100-ml graduated cylinder, the desired amount of salt solution was added and the volume brought to the 80-ml mark with distilled water. Lime slurry was then added to the above mixture giving a final lime concentration of 850-1000 ppm. Mixing was accomplished by inverting the graduates five times. The treated effluent was then allowed to stand undisturbed for a minimum of 15 minutes and the volume of sludge was centrifuging at 9000 rpm for 15 minutes. The clear supernatant was carefully poured off and stored until tested for color. The percentage of removal of color was calculated from the data and the results are given in Table 34. The results show that at 850 ppm lime, 300 ppm $BaCl_2$, and 150 ppm $FeCl_3$ are reasonably optimum quantities for color removal from the untreated caustic extract, whereas in the case of lime-treated caustic extract only $\leq$ 50 ppm $BaCl_2$ and $\leq$ 25 ppm $FeCl_3$ are sufficient to give maximum color removal. (Metal ions should be added before lime addition.)

In the case of NSSC effluents, however, at 1000 ppm lime the percentage of color removal generally increases with increasing amounts of salt concentrations. It seems that "optimum" concentration was not reached in the range studied.

TREATMENT OF MILL WASTES WITH VARYING LIME CONCENTRATION AND CONSTANT METAL ION CONCENTRATION

In this set of experiments lime concentration was varied from 300 to 1500 ppm and ferric- and barium chloride were kept constant at concentrations set by previous experiment.

Forty milliliters of 0.2 percent effluent was mixed with the required amounts of salt solution and lime, the volume was made-up to 80 ml in a 100-ml measuring cylinder and the mixture processed and analyzed as before. The results are given in Table 35.

The data show that $FeCl_3$ is more effective than $BaCl_2$ in the case of all effluents tried. For example, with untreated caustic extract over 96 percent color was removed with 150 ppm $FeCl_3$ and only 300 ppm lime, whereas in the case of $BaCl_2$, 96 percent removal could be reached at 300 ppm $BaCl_2$ and 1500 ppm lime.

Table 34. PERCENT COLOR REMOVAL FROM MILL WASTES BY THE METAL ION-LIME SYSTEM
(Lime Concentration Kept Constant)

Salt concentration, ppm	Caustic extract (850 ppm lime)		NSSC effluent (1000 ppm lime)	
	Untreated	Lime-treated	Untreated	Lime-treated
$BaCl_2$				
0	86.0	67.2	53.3	31.9
50	--	>85.7	--	--
100	91.1	>85.7	58.5	37.5
200	93.0	>85.7	56.7	42.8
250	91.7	>85.7	63.5	40.0
300	94.8	>85.7	60.4	41.7
500	94.9	>85.7	60.4	40.8
1000	93.9	>85.7	62.6	53.4
1250	94.9	>85.7	64.1	59.0
1500	94.8	>85.7	67.2	58.0
$FeCl_3$				
0	86.0	67.2	53.5	31.9
25	94.3	>85.7	64.1	41.3
50	95.2	>85.7	68.4	45.9
75	92.5	>85.7	73.0	49.2
100	94.9	>85.7	74.1	49.2
125	94.5	>85.7	73.7	51.4
150	96.6	>85.7	74.3	54.1
200	96.8	>85.7	79.9	54.5
300	97.8	>85.7	80.7	61.8

$BaCl_2$, 100 ppm = 4.8×10^{-4} moles/l.
$FeCl_3$, 100 ppm = 6.2×10^{-4} moles/l.

The low figure of 300 ppm lime in combination with 150 ppm $FeCl_3$ is much lower than the stoichiometric lime requirement of 1000-1500 ppm in the absence of metal ions. At this concentration (300 ppm) of lime, however, the sludge obtained was very light and hard to settle. Further exploration showed that good settling sludges were obtained, especially when $FeCl_3$ was present, at a minimum lime concentration of about 1000 ppm. The Table 35 further shows that over 50 percent of the color left by conventional lime treatment can be removed by using a $FeCl_3$-lime system.

Table 35. PERCENT COLOR REMOVAL FROM MILL WASTES BY THE METAL ION-LIME SYSTEM
(Metal Ion Concentration Kept Constant)

Lime concentration, ppm	Caustic extract		NSSC effluent	
	Untreated	Lime-treated	Untreated	Lime-treated
$BaCl_2$	300 ppm	100 ppm	300 ppm	1000 ppm
0	0	--	--	--
300	91.7	45.6	18.6	28.0
400	92.6	45.6	25.7	29.6
500	92.7	49.1	27.4	34.5
600	93.3	52.6	51.9	24.1
700	94.1	52.6	53.1	37.9
800	94.6	52.6	55.7	39.4
900	95.0	49.1	56.8	42.5
1000	94.9	52.6	62.2	35.9
1500	95.9	54.4	61.1	40.9
$FeCl_3$	150 ppm	25 ppm	200 ppm	200 ppm
0	$\sim$20.00	--	--	--
300	96.5	54.4	41.7	31.4
400	97.5	54.4	58.9	47.1
500	97.8	57.9	67.0	40.9
600	97.9	54.4	--	52.7
700	98.1	52.6	--	50.3
800	98.3	52.6	73.4	57.3
900	98.3	50.9	71.0	58.8
1000	98.3	54.4	73.3	57.9
1500	98.3	59.7	73.9	48.9

$BaCl_2$, 100 ppm = 4.8×10^{-4} moles/l.
$FeCl_3$, 100 ppm = 6.2×10^{-4} moles/l.
Lime, 100 ppm = 13.5×10^{-4} moles/l.

In the case of NSSC effluent, conventional stoichiometric lime treatment has been found to remove about 64 percent of the color (see Appendix V); this percentage removal figure can be achieved using about half the stoichiometric lime required with 200 ppm $FeCl_3$. In this case also over 50 percent color can be removed from the lime-treated effluent.

STATISTICAL ANALYSIS (REGRESSION ANALYSIS)

In any system in which variable quantities change, it is of interest to examine the effects that some variables exert (or appear to exert) on others. There may be in fact a simple functional relationship between variables; but most often the functional relationship which is too complicated to grasp or describe in simple terms. If this is the case, we may wish to approximate this functional relationship by some simple mathematical function, such as a polynomial, which contains the appropriate variables and which approximates the true function over some limited ranges of the variables involved. By examination of such a function we may be able to learn more about the underlying true relationship and to appreciate the separate and joint effects produced by changes in certain important variables.

Even where no sensible physical relationship exists between variables, we may wish to relate them by some mathematical equation. The equation may be physically meaningless, but it may nevertheless be extremely valuable for predicting the values of some variables from knowledge of others. The details of this analysis are given in the experimental part of this report.

The data obtained by previous experiments (Tables 34 and 35) were analyzed using the standard regression analysis techniques. The results of the analysis relate the change in percentage of color removed to the amount of lime and metal ion present. The three regression equations obtained are given in their respective tables, 36, 37, and 38. The theoretical values of color removal obtained by regression analysis are plotted against experimental values in Figures 56, 57, and 58.

The data from Table 34, where metal ion concentration was varied and lime concentration kept constant, were analyzed to obtain constants shown in Tables 36 and 37. Analysis showed that both iron and barium contribute significantly to the removal of effluent color. The presence of the b_2 term in both equations indicates slight deviation from a linear effect. Lime has a "constant" effect on color removal when iron is present and a "nonconstant" effect when barium is present (because of the presence of the b_3 slope). In other words, when barium is used with lime, both barium and lime can be added to significantly change the color removal effect.

Table 36. EFFECT OF FERRIC CHLORIDE CONCENTRATION ON LIME TREATMENT OF KRAFT BLEACH EFFLUENTS (CAUSTIC STAGE)

Model: $\text{Percent} = b_0 + b_1[\text{FeCl}_3] + b_2[\text{FeCl}_3]^2 + b_3[\text{lime}] + b_4[\text{lime}]^2$

Regression terms	Regression coefficient	Standard error
b_0, %	92.17	--
b_1	0.048388	0.005700
b_2	-0.000097	0.000052
b_3	--	--
b_4	--	--
r^2, %	54.0	

Note: The regression coefficients b_1, b_2, b_3, b_4, give the response per unit change in the variable. In the above table terms b_3 and b_4 are not significant.

b_0 = Average percentage color removal by $FeCl_3$ over the range studied.

r^2 = Percentage total variability of color removal explained by the above equation.

The values labeled r^2 indicate the percentages of total variation of color removal which have been explained by the regression equations shown. The lower percentage values (54 and 60 percent, Tables 36 and 37, respectively) are not very good and indicate the existence of potentially sizable deviations between predicted and experimental color removal values. The 96 percent value for the model in Table 38 is much better.

The data from Table 35, where metal ion concentration was kept constant and lime concentration varied, were used to obtain the constants shown in Table 38. A dummy variable was introduced in the calculations to indicate the different metal ions present. Results showed that lime has a significant effect on color removal and that this effect is nonlinear.

Table 37. EFFECT OF BARIUM CHLORIDE CONCENTRATION ON LIME TREATMENT OF KRAFT BLEACH EFFLUENTS (CAUSTIC STAGE)

Model: Percent = $b_0 + b_1[\mathrm{BaCl_2}] + b_2[\mathrm{BaCl_2}]^2 + b_3[\mathrm{lime}] + b_4[\mathrm{lime}]^2$

Regression terms	Refression coefficient	Standard error
b_0, %	89.11	--
b_1	0.007683	0.003579
b_2	-0.000004	0.000002
b_3	0.003208	0.000944
b_4	--	--
r^2, %	60.0	

Note: The regression coefficients b_1, b_2, b_3, b_4, give the response per unit change in the variable. In the above table term b_4 is not significant.

b_0 = Average color removal by $\mathrm{BaCl_2}$ over the range studied.

r^2 = Percentage total variability of color removal explained by the above equation.

Table 38. EFFECT OF LIME CONCENTRATION ON COLOR REMOVAL WITH CONSTANT LEVELS OF METAL IONS

Model: Percent = $b_0 + b_1[\mathrm{lime}] + b_2[\mathrm{lime}]^2 + b_3[X]$

where X = 0 when $\mathrm{FeCl_3}$ is present, and
= 1 when $\mathrm{BaCl_2}$ is present.

Regression terms	Regression coefficient	Standard error
b_0	94.21	--
b_1	0.007599	0.000416
b_2	-0.000003	0.000001
b_3	-4.03	0.23
r^2	96.0	

Note: The regression coefficients b_1, b_2, b_3, give the change in response per unit change in the variable.

b_0 = Average percentage color removal by lime over the range studied.

r^2 = Percentage total variability of color removal explained by the above equation.

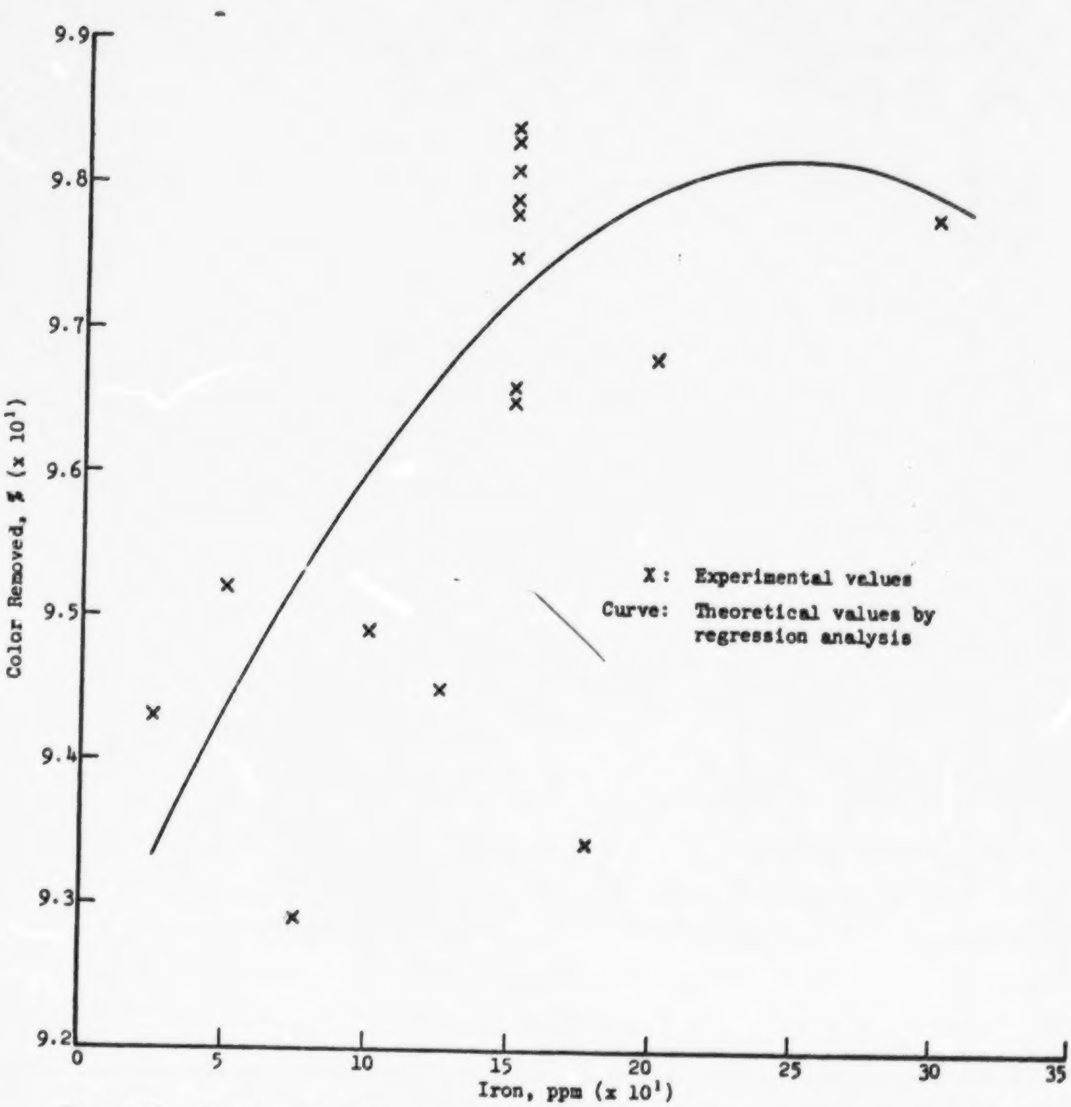

Figure 56. Effect of $FeCl_3$ concentration on color removal. Lime concentration was kept constant. (Color removal values at 150 ppm $FeCl_3$ from Table 40 have also been plotted here)

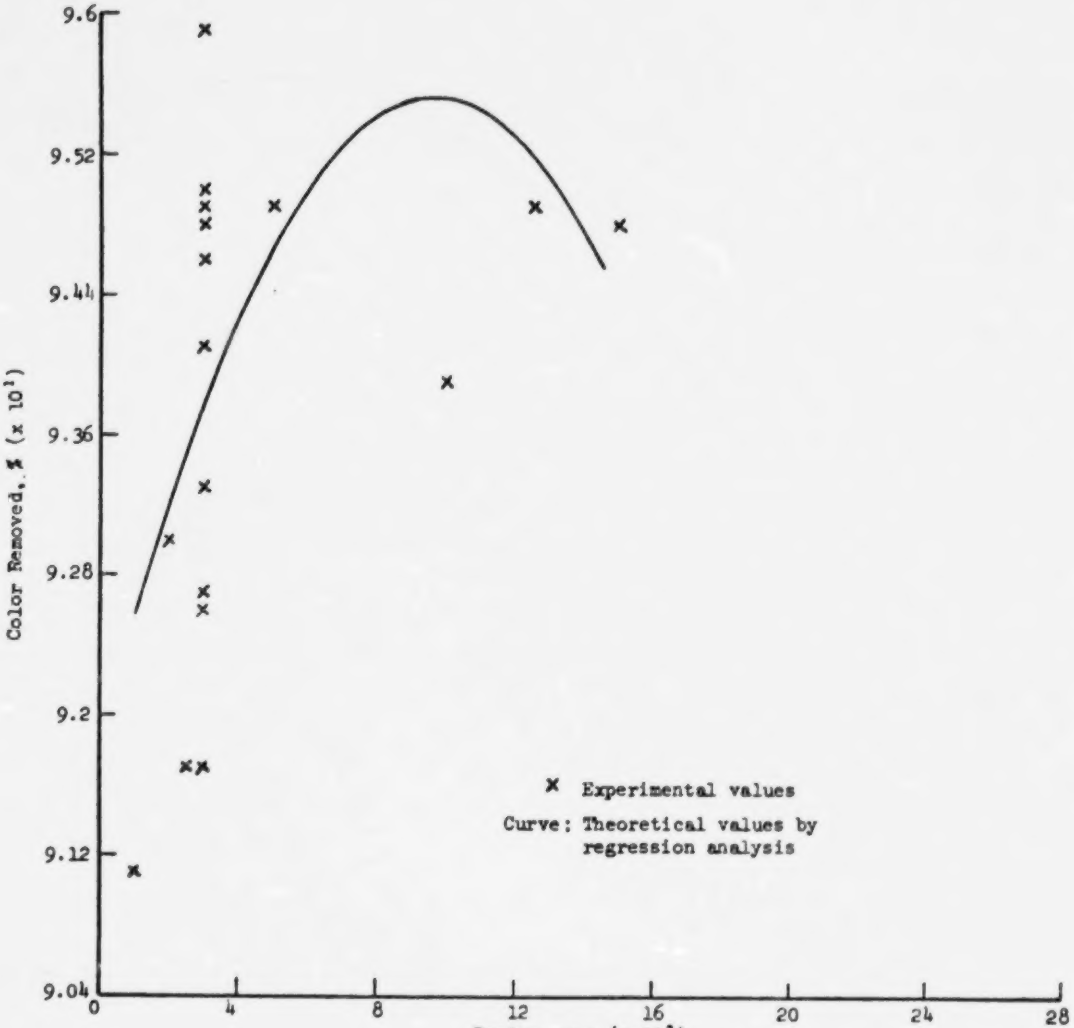

Figure 57. Effect of $BaCl_2$ concentration on color removal. Lime concentration was kept constant. (Color removal values at 300 ppm $BaCl_2$ from Table 40 have also been plotted here)

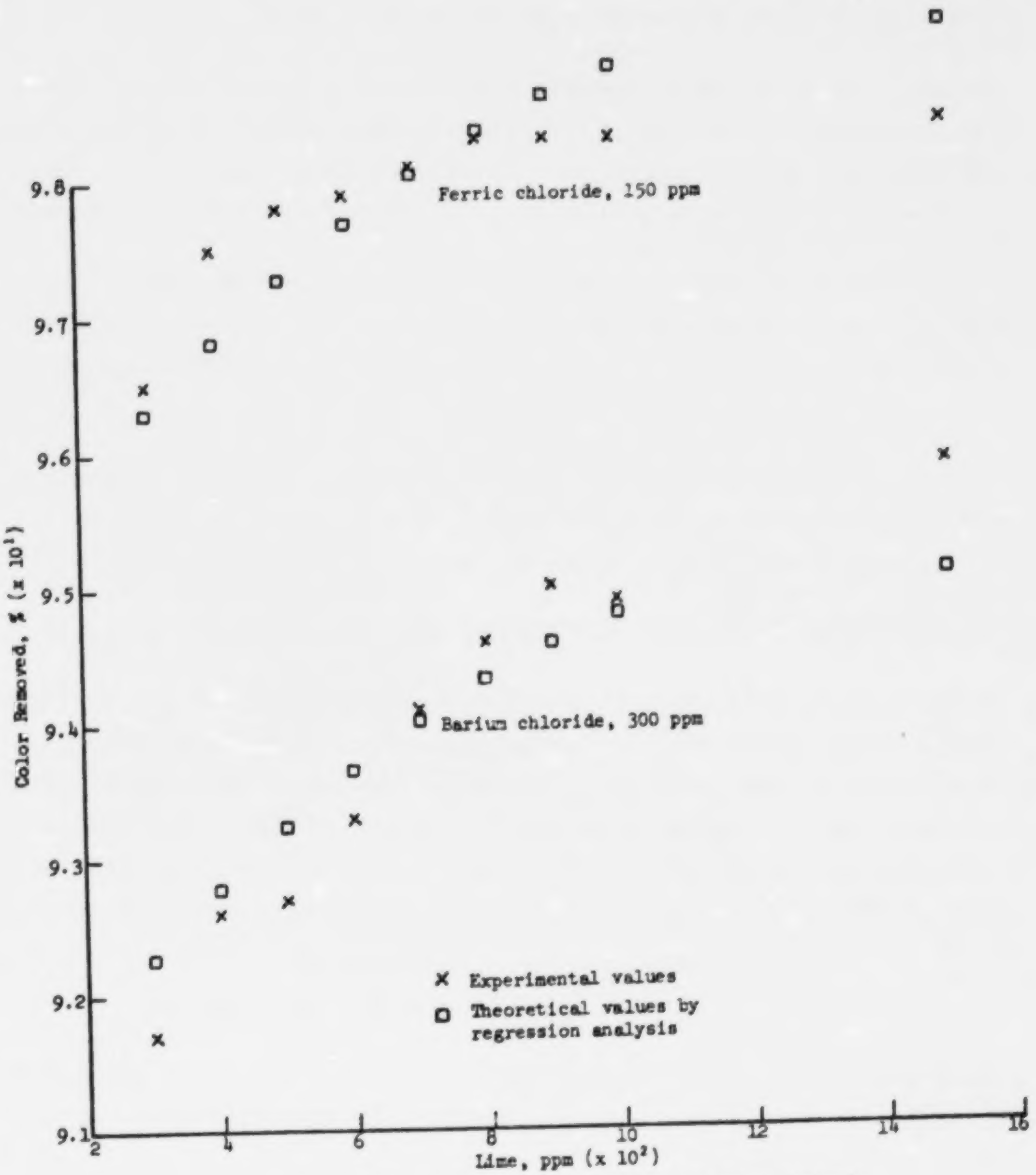

Figure 58. Effect of lime concentration on color removal. Metal ion concentration kept constant

The presence of b_3 constant indicates that the use of barium in place of iron will result in a loss of 4 percentage units of color removal.

The analysis of the data suggested that iron is a more effective color-removing agent than barium in the lime treatment of mill effluents (Figure 58). The analysis shows that when the amount of iron is held constant and lime varied, a good estimate of the effect of lime can be made.

Figures 56 and 57 show large deviation from the regression curve (theoretical curve) and suggest that when discussing the expected percentage color removal due to either metal ions, a range would be more useful than a definite prediction.

To provide information about the independence of the effect of the two additives (lime and iron) it was thought that a series be run in which the amounts of both iron and lime be varied.

TREATMENT OF MILL EFFLUENT WITH VARYING LIME AND $FeCl_3$

Designed experiments were performed to study the effect of lime treatment on kraft bleach effluent in the presence of metal ions ($FeCl_3$). The purpose of this study was to determine the effect of these additives on the amount of color removed from the effluent samples, and also to determine whether or not the effects of the two additives are independent of each other. The following levels of additives were studied.

Lime, ppm: 1000, 2000, 18,000
$FeCl_3$, ppm: 0, 25, 50, 100, 200, 300, 500, 800

The levels of each variable were run once with all levels of the other, giving a total of twenty four experiments. The results obtained are given in Table 39.

The effect of $FeCl_3$ on sludge volume at different levels of lime is depicted in Figure 59. Lime concentrations of 1000 and 18,000 ppm and $FeCl_3$ concentration of more than 100 ppm give denser sludges than those at 2000 ppm. In fact, sludge obtained at 18,000 ppm lime is the most dense indicating better settling properties.

Table 39. LIME TREATMENT OF KRAFT BLEACH CAUSTIC EXTRACT IN THE PRESENCE OF METAL ION

Experiment no.	$FeCl_3$, ppm	Lime, ppm	Sludge vol., ml	Final pH	Color units	Absorbance, 280 nm	Absorbance, 480 nm	TOC, mg/1	BOD, mg/1
Untreated caustic extract				8.83	4,397	9.45	2.12	220	47
1	0	1,000	6.2	11.58	820	2.53	0.38	73.5	44
2	25	1,000	8.2	11.50	806	2.57	0.36	74.5	45
3	50	1,000	8.2	11.42	627	2.20	0.32	63.8	47
4	100	1,000	8.5	11.42	440	1.60	0.19	48.3	41
5	200	1,000	13.3	11.49	377	1.42	0.19	52.0	36
6	300	1,000	14.4	11.50	370	1.44	0.21	56.5	34
7	500	1,000	22.0	11.40	186	0.81	0.09	42.0	30
8	800	1,000	30.1	11.32	196	0.84	0.09	37.8	28
1	0	2,000	6.2	11.79	561	2.00	0.29	69.0	36
2	25	2,000	7.0	11.70	528	1.83	0.23	54.0	36
3	50	2,000	7.3	11.70	462	1.74	0.25	59.5	35
4	100	2,000	9.7	11.70	361	1.42	0.20	54.5	33
5	200	2,000	14.1	11.70	294	1.10	0.13	44.8	31
6	300	2,000	19.1	11.71	209	0.97	0.12	40.5	30
7	500	2,000	33.5	11.78	141	0.70	0.10	30.8	26
8	800	2,000	62.0	11.73	111	0.50	0.05	28.0	23
1	0	18,000	8.9	11.98	292	1.01	0.15	43.0	32
2	25	18,000	8.7	11.99	226	0.97	0.14	45.0	32
3	50	18,000	9.0	11.98	220	0.87	0.11	49.3	29
4	100	18,000	9.4	12.00	180	0.82	0.09	40.3	30
5	200	18,000	11.2	12.01	162	0.68	0.06	35.0	30
6	300	18,000	12.2	12.01	119	0.51	0.04	40.8	25
7	500	18,000	14.3	12.01	80	0.40	0.04	27.0	25
8	800	18,000	16.8	12.00	58	0.34	0.02	24.8	23

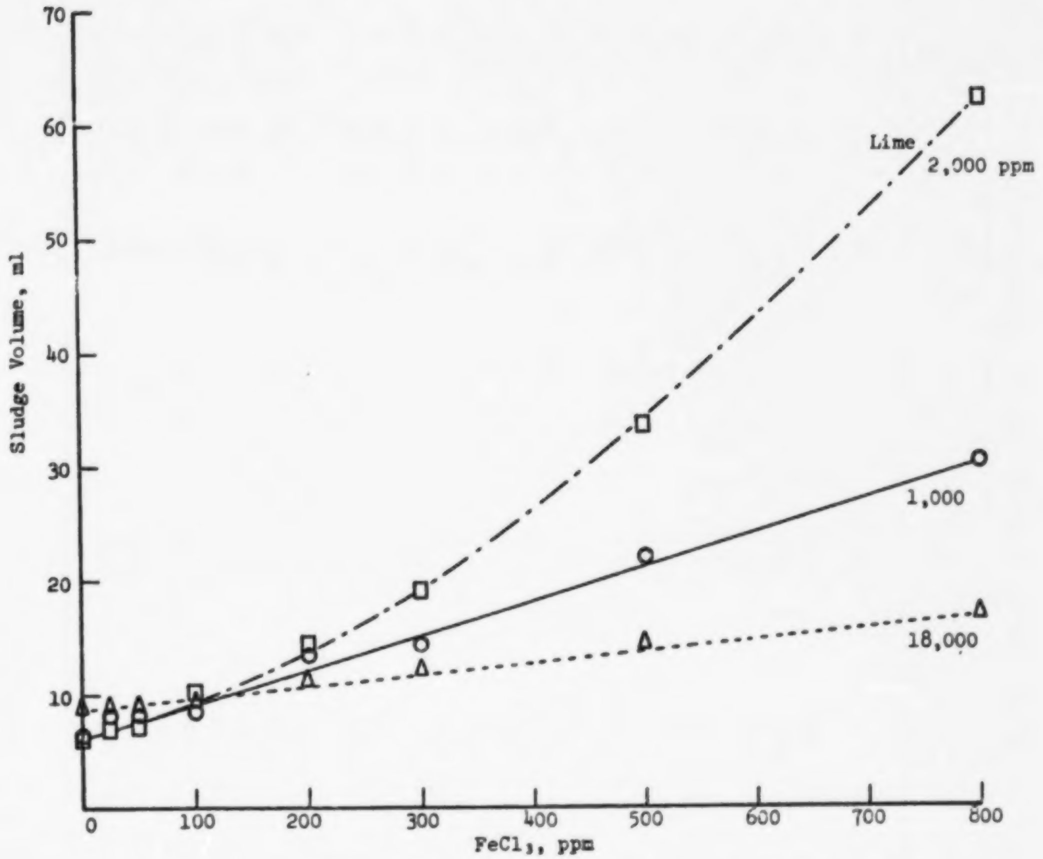

Figure 59. Effect of ferric chloride and lime on sludge volume

The percentage color removal based on results in Table 39 are given as "actual" data in Table 40. The data in Table 40 were analyzed using standard regression analysis techniques similar to the one used earlier. The regression equation which was obtained from the data in Table 40 is given in Table 41. The last term (b_5) in the regression equation indicates a lack of independence between lime and the metal ions and their effect upon the color removal. In other words, it cannot be predicted how much color one may remove by adding 500 ppm $FeCl_3$ without knowing how much lime will be added also. This fact has also been demonstrated by Figure 60. Had the effect of these two variables been independent, all curves would have shown similar trends and slopes.

Table 40. PERCENT COLOR REMOVAL BY LIME IN THE PRESENCE OF METAL IONS

$FeCl_3$ concentration ppm	Lime concentration, ppm					
	1000		2000		18,000	
	actual[a]	cal[b]	actual[a]	cal[b]	actual[a]	cal[b]
0	81.4	83.8	87.2	87.3	93.4	93.3
25	81.7	84.7	88.0	88.1	94.9	93.9
50	85.7	85.5	89.5	88.9	95.0	94.5
100	90.0	87.1	91.8	90.5	95.9	95.5
200	91.4	89.8	93.6	93.1	96.3	97.3
300	91.6	92.0	95.2	95.2	97.3	98.5
500	95.8	94.8	96.8	98.0	98.2	99.5
800	95.5	95.4	97.5	98.4	98.7	97.2

[a] Experimental values.
[b] Calculated values by regression analysis.

Using the regression equation (Table 41) and the actual levels of additives, the "calculated" percentage color removal values are obtained (see Table 40). The agreement between the actual and the calculated data is extremely good for all levels (Figure 61). The correlation for this equation, i.e., the percentage variation, r^2, in color removal explained by the regression is 93% (Table 41).

Table 41. EFFECT OF VARYING LIME AND METAL ION CONCENTRATION ON COLOR REMOVAL (REGRESSION EQUATION)

Model: $\text{Percent} = b_0 + b_1[FeCl_3] = b_2[FeCl_3]^2 + b_3[\text{lime}] + b_4[\text{lime}]^2 + b_5[FeCl_3][\text{lime}]$

Regression terms	Regression coefficient	Standard error
b_0	80.05	--
b_1	35.03×10^{-3}	4.239×10^{-3}
b_2	-0.025×10^{-3}	0.00514×10^{-3}
b_3	3.99×10^{-3}	0.8824×10^{-3}
b_4	$-0.0001809 \times 10^{-3}$	0.000045×10^{-3}
b_5	$-0.0005994 \times 10^{-3}$	0.000150×10^{-3}
r^2	93.0	

Note: The regression coefficients b_1, b_2, b_3, b_4, b_5, give the change in the response per unit changes in variable.
b_0 = Average percentage color removal over the range studied.
r^2 = Percentage total variability of color removal explained by the above equation.

A comparison of regression coefficients obtained earlier (Tables 36 and 37) and now (Table 41) is made in Table 42. This table shows that with the exception of the constant for the quadratic effects, the regression coefficients of the present work are in line with those obtained in the earlier work. The linear terms for both lime and $FeCl_3$ are within the statistical limits of acceptability. The changes in the quadratic terms, however, would seem to be due to the presence of the interaction of $FeCl_3$ and lime.

Similar experiments run on the lime-treated caustic extract as run on the untreated caustic extract (see Table 39) indicated that over 80 percent of the color, which was left by conventional lime treatment process, can be removed using 500 ppm $FeCl_3$ and 1000 ppm lime. At lower $FeCl_3$ concentrations (less than 150 ppm) and 1000 ppm lime only, 65-70 percent color was removed.

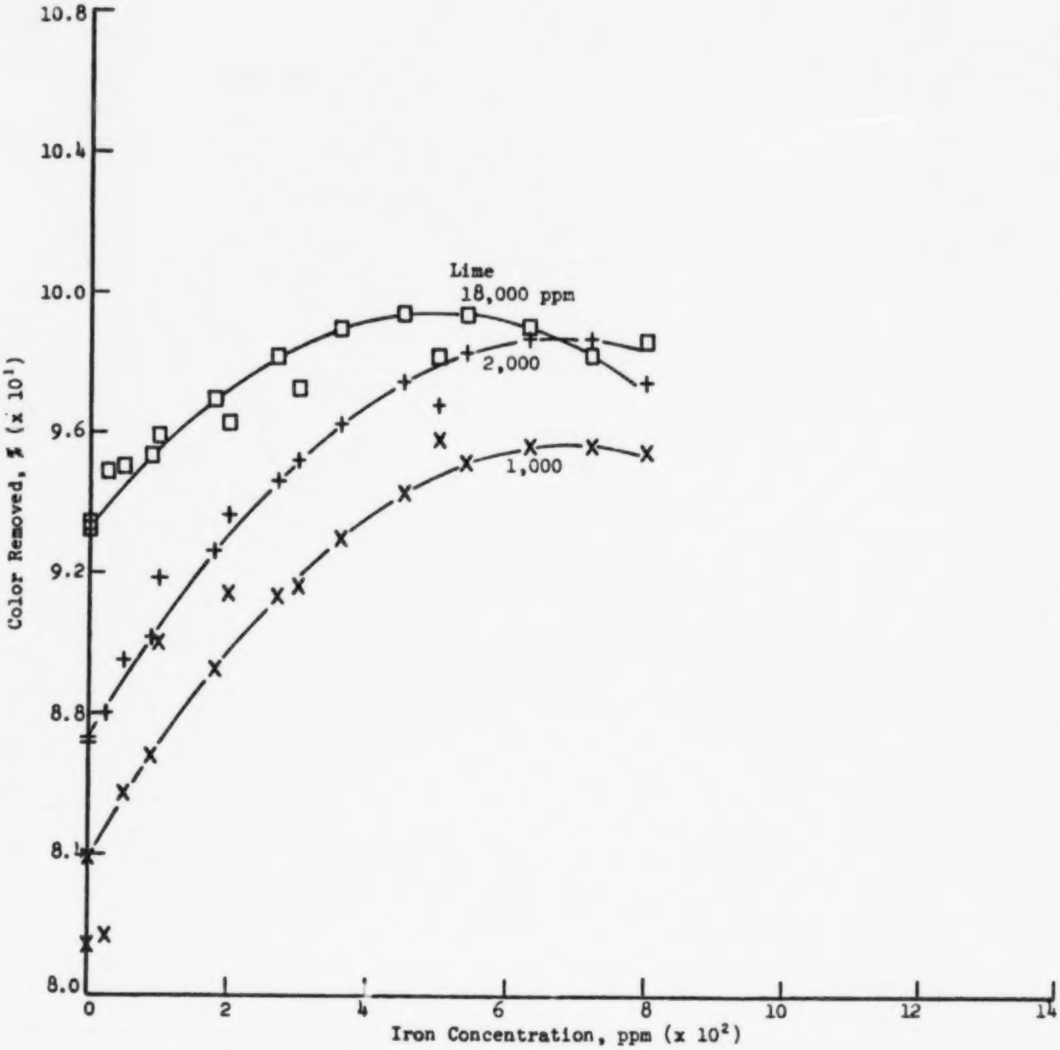

Figure 60. The interactive behavior of lime and metal ions on color removal

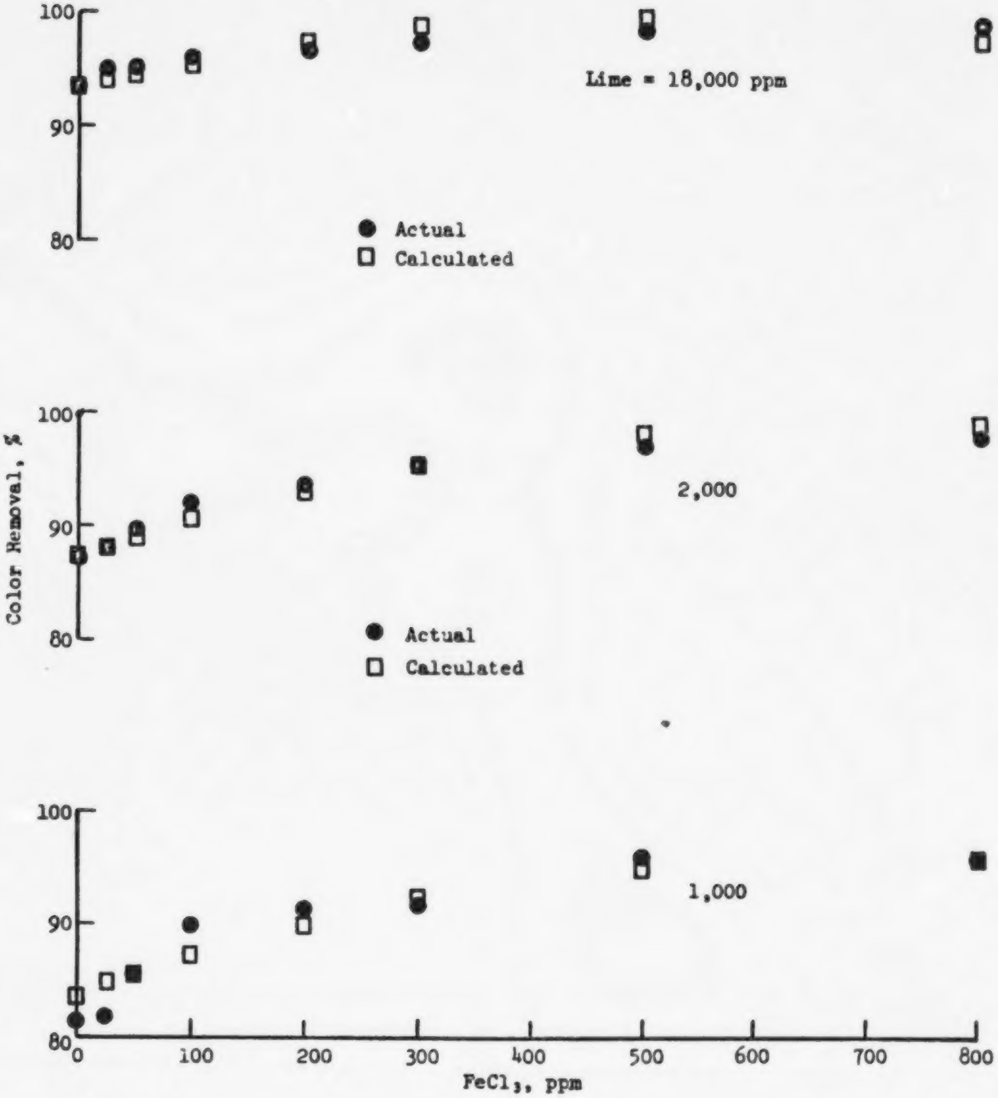

Figure 61 Percentage of color removal by lime in the presence of metal ions

Table 42. COMPARISON OF REGRESSION COEFFICIENTS

	Regression coefficients	
	From Tables 35, 36	From Table 40
Linear $FeCl_3$, ppm	48.39×10^{-3}	35.03×10^{-3}
Linear lime, ppm	7.60×10^{-3}	3.99×10^{-3}
Quadratic $FeCl_3$, ppm	-0.097×10^{-3}	-0.025×10^{-3}
Quadratic lime, ppm	-0.003×10^{-3}	-0.000181×10^{-3}
Interaction[a], ppm	—NA—	-0.00056×10^{-3}

NA = not available.

[a] Interaction of $FeCl_3$ and lime.

The statistical analysis suggested that iron is a more effective color-removing agent than barium in the lime treatment of mill effluent. This study further suggests that some interaction between lime and $FeCl_3$ is present resulting in better color removal then when either of the two is used separately. In other words a "synergistic" effect exists.

SECTION VII

EXPERIMENTAL

PROCESSING AND FREEZE-DRYING OF WASTES

Untreated and lime-treated colored samples were concentrated under reduced pressure to one-tenth of their original volume. (Untreated samples, if concentrated further, were very difficult to freeze-dry.) Most of the calcium, especially in the lime-treated samples, was precipitated by carbonating the samples to a pH of 10.2. The carbonated samples were then centrifuged in the beta-centrifuge at 9000 rpm for 15 minutes. This speed and time was sufficient to give clear solutions. If, in some cases, slight turbidity was still present, these samples were filtered through a Millipore filter paper. The pH of the solution was checked at every stage. The colored but clear solutions were frozen in strong glass containers (centrifuge bottles) and dried under high vacuum. This freeze-dried material formed a low density powder and was readily soluble in water. The dried samples could be kept in airtight bottles for longer periods without any significant change.

ISOLATION OF ACID-INSOLUBLE COLOR BODIES

Freeze-dried solids of the untreated waste (14.3 g od basis) were dissolved under mechanical stirring in 60 ml of water and approximately 17 g of clean cellulose powder (Whatman standard grade) was suspended in the solution. The stirring was continued and the pH was adjusted to 1.0 with strong hydrochloric acid (1 vol. concentrated acid to 2 vol. of distilled water). The acidified mixture was filtered through a precoat of about 4 g of cellulose powder on a Buchner funnel and the filter cake was washed with a total of 50 ml of water in small portions. When the filtrate was just acid to Congo Red paper, some of the precipitate peptized and formed a cloudy filtrate. The cloudy filtrate was mixed with about 3 g of acid-washed Fibra-Flo 11C (Johns-Manville filter aid), the mixture was filtered on a thin precoat of Fibra-Flo on a small Buchner funnel, and the filter cake was washed with water.

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Both the cellulose powder and the Fibra-Flo filter cakes were separately extracted with 50 percent aqueous ethanol. The alcohol was evaporated from the combined solution at reduced pressure whereupon a finely divided precipitate formed; the slurry containing this precipitate was subsequently freeze-dried, and designated as "acid-insolubles." The aqueous filtrate contained the "acid-soluble" material.

ISOLATION OF ACID-SOLUBLE COLOR BODIES

The acid-soluble fractions obtained during acidification of mill wastes were recovered and fractionated using Rohm & Haas Co.'s Amberlite XAD-8 resin (polystyrene cross-linked with divinyl benzene).

The acid-soluble solutions were first passed through a 240 ml bed of Amberlite XAD-8 resin. The column was eluted first with water and then with aqueous ethanol (1:1 water — 95 percent ethanol mixture). The eluate was actually collected in seven fractions but the last four fractions (eluted with aqueous ethanol) were combined to give four final fractions. Each fraction was made alkaline with sodium hydroxide to pH about 9.0 (ethanol was removed under reduced pressure).

The first fraction contained material which passed through the column (unadsorbed) with the original solution. A floc similar to that of ferric hydroxide was noticed when this fraction was made alkaline, and the floc was separated by filtration.

The second fraction contained material which was held on the column initially, but was readily eluted from the column with water. Upon alkalization this fraction deepened in color and was more highly colored than the first fraction.

The third fraction was an intermediate fraction and was collected until the eluate was neutral to Congo Red.

The fourth and the final fraction contained material eluted with aqueous ethanol.

It should be kept in mind that the fractionation was not sharp, and thus each fraction could contain some material similar to that found in the previous fraction.

FRACTIONATION OF COLOR BODIES

Two types of Bio-Gels (Bio Rad Co.) were used for this purpose. Bio-Gel P-2 (exclusion limit 2600) and P-60 (exclusion limit 60,000) were hydrated in distilled water and separately packed in 2.5 x 200 cm and 2.5 x 100 cm glass columns, respectively. The complete apparatus used for fractionation is shown in Figure 62.

The volume of the solutions used for fractionation was less than 3 percent of the void volume of the column (void volume, Vo, = total bed volume x 0.38). A measured quantity of the solution was added to the top of the column. A glass fiber filter was used on the gel so that upon addition of the solution, the gel surface was not disturbed. The eluate was allowed to flow into an automatic collecting device and the collector timer and the UV-cord recorder were started. When the solution dropped to just below the surface of the gel, one milliliter of distilled water was added to the column and elution continued. When the level was again slightly below the gel, more distilled water was added and the column was then connected to the constant head water reservoir through a filter and a flowmeter. The elution rate (0.2-0.3 ml/min) was controlled by a teflon stopcock with a needle adjust. Fractions were collected every 30 minutes. At the end of fractionation, which took three to four days, the collected fractions were combined according to the number of peaks on the UV recorded chart. The combined fractions were freeze-dried and used for study. (Aliquots of the fractions were taken for color, TOC, and absorbance before freeze drying.)

COLOR MEASUREMENT

Color was measured according to the platinum cobalt standard method of the American Public Health Association (APHA)[18]. The only modification of the method was the use of a noncarbonate buffer for pH adjustment to

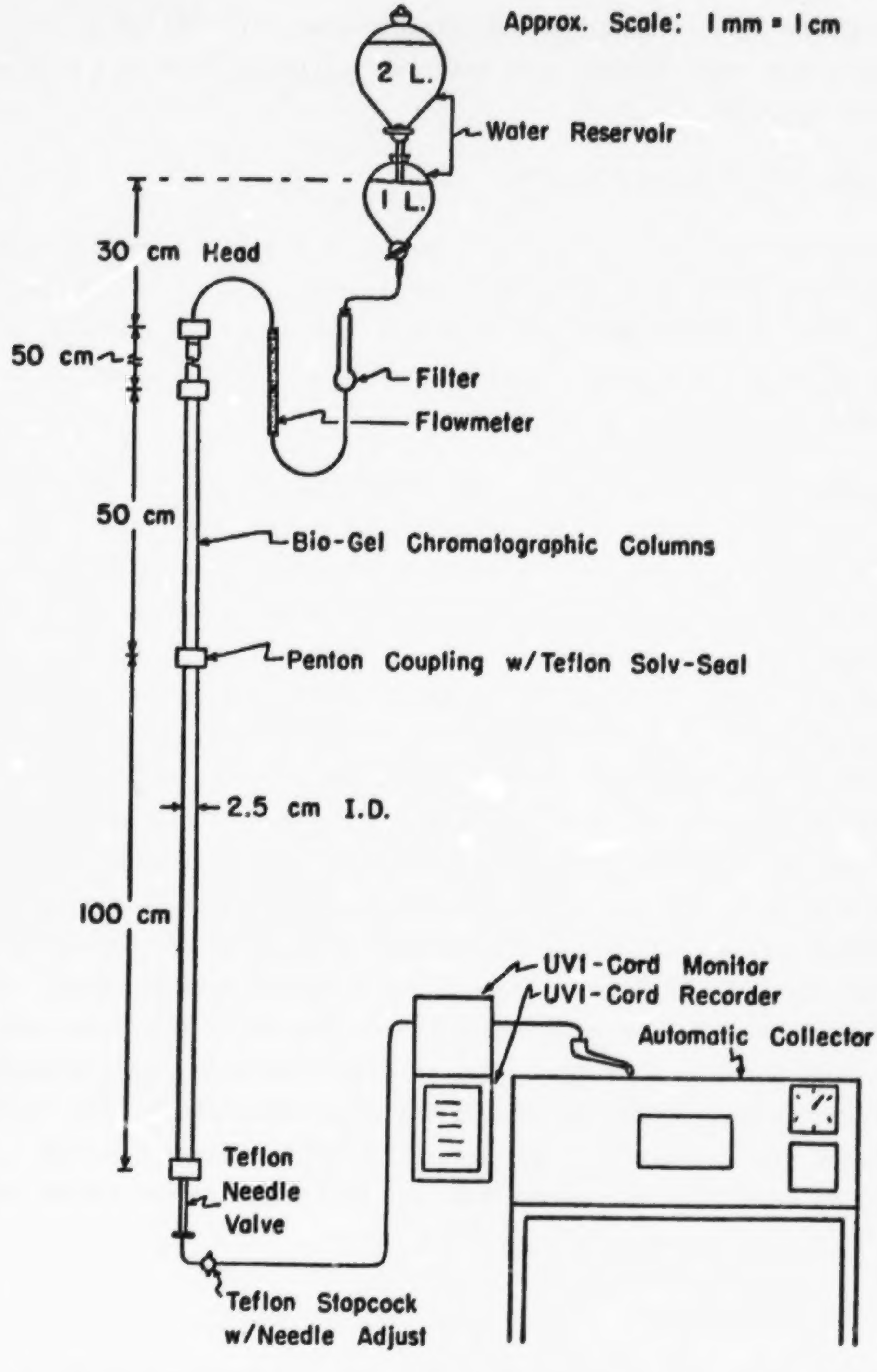
Approx. Scale: 1 mm = 1 cm
2 L.
1 L.
Water Reservoir
30 cm Head
50 cm
Filter
Flowmeter
50 cm
Bio-Gel Chromatographic Columns
Penton Coupling w/Teflon Solv-Seal
2.5 cm I.D.
100 cm
UVI-Cord Monitor
UVI-Cord Recorder
Automatic Collector
Teflon Needle Valve
Teflon Stopcock w/Needle Adjust

Figure 62. Diagram of Gel Permeation Chromatography Apparatus

7.6. It was necessary to have color values at a constant pH of 7.6, because color was found to be pH dependent. Most natural waters have a pH range close to 7.6.

It should be noted that the color unit is a measure of color intensity. When it has been necessary to refer to the total amount of colored material in a solution this has been called "total color" and is the product of the color units and the volume of the solution.

ABSORBANCE MEASUREMENT

The samples used for color measurement were also used for absorbance measurement at desired wavelengths on the Beckman DU Spectrophotometer. The values obtained were multiplied by the dilution factor to give absorbance of the concentrated solutions. Absorptivity was calculated by dividing the absorbance values by concentration in grams per liter.

DETERMINATION OF SOLIDS

Total solids were determined by evaporation of a measured volume of waste at 105°C overnight. The resultant weight of solids was expressed in milligrams per liter (mg/l) of waste.

Fixed and volatile solids were determined by igniting the total solids at 600°C in an electric muffle furnace to constant weight, usually requiring one hour. The loss on ignition is reported as mg/l volatile and the residue as mg/l fixed solids.

METHOXYL CONTENT

Methoxyl content was determined by TAPPI Method T 2 m-60.

PHENOLIC HYDROXYL CONTENT

Phenolic hydroxyls content was determined by the Goldschmid method[19] using ultraviolet spectrophotometry.

TOTAL ORGANIC CARBON (TOC)

The Process Carbonaceous Analyzer (Bechman and Co.) was used for this purpose. Because this instrument gives only total carbon, it was modified to give TOC by the indirect method.

Based on new TOC analyzers, one combustion tube was filled with Quartz beads saturated with concentrated phosphoric acid. Total inorganic carbon was first estimated by injecting samples in the H_3PO_4-combustion tube at 175°C. This tube was then replaced by the regular combustion tube containing the catalyst and total carbon was estimated by injecting samples in catalyst-tube at 950°C. The difference between total carbon and total inorganic carbon gave TOC.

Twenty-three microliters of the specimens were injected at 3 to 5-minute intervals and an average reading was thus obtained from which the "blank" reading was subtracted to give the TOC value in mg/l.

The "blank" consisted of all the ingredients listed above minus the sample and was handled in the same manner as the sample.

In addition to the precautions listed in the operating manual, the following precautions are recommended for accurate results.

a. The injection syringe should be checked often for burrs, cracks, etc., which cause particles from the rubber cap to drop into the combustion tube thus giving high readings.
b. A constant slow needle insertion and retraction is essential to prevent "popping" of the combustion chamber rubber cap.
c. Combustion chamber rubber cap should be replaced often.
d. Tygon tubing close to the condenser, filters, and glass combustion chamber dome should be cleaned often.

DETERMINATION OF MOLECULAR WEIGHTS

Due to large number of samples to be analyzed, the "conventional sedimentation equilibrium method"[14] was considered impractical and the "short column sedimentation equilibrium method" was used. An effective way to reduce operating times is to shorten the fluid column in the centrifuge cell. In the "short column method" samples columns are 1 mm or less compared to 3 mm of the "conventional method." The time for equilibrium was reduced from 24 hours to 3 hours by using the 1-mm column.

Although providing the time advantage as well as simplified computations, "short columns" result in only single value for molecular weight and thus little information concerning the polydispersity or nonideality is available. The values obtained are apparent weight average molecular weights for polydisperse solutes. Normally this procedure has a precision of about 3 percent; however, for most of this work especially due to low molecular weights of most samples, the precision is probably much lower.

For calculation of molecular weights the quantity required from the equilibrium run is the concentration gradient at the midpoint of the solution column usually obtained directly from schlieren patterns. However, at the higher concentrations required for schlieren optics, the colored solutions resulted in photos which were not measurable. The more sensitive interference optical system allowed use of less concentrated solutions with less color and provided reasonably clear fringe patterns. In this case, the slope of the interference fringes at the midpoint of the solution column is the concentration gradient. It is assumed, in this method, that the solute concentration at the midpoint is equal to the initial concentration. The initial concentration must also be determined. This is done in a separate centrifuge run measuring the total fringe shift (fringe number) across a synthetically formed boundary. Sample concentrations were normally 0.2 percent (in H_2O) although a few were run at 0.1 percent due to color problems. Solutions prepared from freeze-dried samples were adjusted to pH 9.0-9.5. Equilibrium runs were made in a 6-channel cell which accommodates three samples per run.

The densities of the solutions were measured according to the method described by Bauer[20] and plotted against their respective concentrations in g/ml. A straight-line plot was developed and the partial specific volume, $\overline{V}$, was calculated from the straight-line relationship using the Equation

$$\overline{V} = \frac{1}{do} - [(\frac{1}{x})] (\frac{d - do}{do})$$

where

x = concentration, g/ml
do = density of solvent
d = density of solution.

The calculations were made by the following equations and a computer program (SHOCOL) was written to handle the raw data.

$$M = \frac{RT}{(1-\overline{v}\rho)\omega^2} \frac{1}{r_{mid}\ c_o} (\frac{dc}{dr})_{mid}$$

m = molecular weight
R = 8.314 x 10^7 (Universal gas constant)
T = 303 (temperature)
v = partial specific volume
ρ = solution density
r_{mid} = radial distance to solution midpoint, cm
c_o = initial solution concentration
$(\frac{dc}{dr})_{mid}$ = concentration gradient at solution midpoint
ω = angular velocity, radians per second.

The initial rotor speed in all runs was 42,040 rpm which is near the recommended maximum speed for the 6 channel cell. After equilibrium was achieved (usually less than 3 hours) a photograph was taken and the rotot speed was reduced to 3 lower speeds allowing time for equilibrium to be reached at each rpm. The analysis then results in apparent molecular weights (M_w) at each of 4 rotor speeds for each sample.

Plots were then made of $1/M_w$ versus angular velocity with linear extrapolation to $\omega^2 = 0$. Comparisons in molecular weights could then be made with the effect of rotor speed eliminated.

In most cases the plots had only a slight slope. However, for some fractions, especially A_1, M_w were highly dependent on ω^2, apparently due to solute polydispersity. The much higher M_w (at $\omega^2 = 0$) for A_1

fractions in general were confirmed by analysis of the photographs by the conventional equilibrium method. An extension of this procedure would be to run each sample as described at several concentrations and plot $1/M_w$ at $\omega^2 = 0$ versus concentration to eliminate concentration effects also.

REGRESSION ANALYSIS[21]

The analysis was performed to study the effect of one variable on other as per example given below:

Linear Regression, Case Problem

Let us assume that the regression line (the mathematical equation) of a variable Y on a variable X has the form $\beta_o + \beta_1 X$. Then we can write the linear, first order model

$$Y = \beta_o + \beta_1 X + \varepsilon \qquad (1)$$

That is, for a given X, a corresponding observation Y consists of the value $\beta_o + \beta_1 X$ plus an amount ε, the increment by which an individual Y may fall off the regression line.

Equation (1) is the model of what we believe. We begin by assuming that it holds; we will inquire later if it does hold. β_o and β_1 are called the parameters of the model. When we say that a model is linear or nonlinear, we are referring to the linearity or nonlinearity in the parameters. The value of the highest power of an independent variable in the model is called the order of the model. For example

$$Y = \beta_o + \beta_1 X + \beta_{1,1} X^2 + \varepsilon \qquad (2)$$

is a second-order (in X) linear (in the β's) regression model.

The values β_o, β_1, and ε are unknown in Equation (1) and in fact ε would be difficult to discover since it changes for each observation Y. β_o and β_1 however remain fixed. Although we cannot find them exactly without examining all possible occurrences of Y and X, we can use information from an experiment in which we measure a subset of the values, and obtain estimates, b_o and b_1 of β_o and β_1. We then can write

$$Y' = b_o + b_1X \tag{3}$$

where Y' denotes the predicted value of Y for a given X. Equation (3) is then used as a predictive equation; substitution for a value of X would provide an estimate of the true mean value of Y for that X.

Linear Regression, Solution

Suppose we have available n sets of observations (X_1, Y_1), (X_2, Y_2), ..., (X_n, Y_n). Then we can write [from Equation (1)]

$$Y_i = \beta_o + \beta_1X_1 + \varepsilon_i \tag{4}$$

The sum of squares of the deviations from the true line is

$$S = \Sigma e_i{}^2 = \Sigma(Y_i - \beta_o - \beta_1X_i)^2 \tag{5}$$

We will choose our estimates b_o and b_1 to be values which when substituted for β_o and β_1 in Equation (5) produce a minimum value of S. We determine b_o and b_1 by differentiating Equation (5) first with respect to β_o and then with respect to β_1 and setting the result equal to zero. We have then

$$\frac{\partial S}{\partial \beta_o} = -2\Sigma(Y_i - \beta_o - \beta_1X_i) \tag{6}$$

$$\frac{\partial S}{\partial \beta_1} = -2\Sigma(Y_i - \beta_o - \beta_1X_i)X_i \tag{7}$$

Substitution of b_o and b_1 for β_o and β_1 then gives the following equations to solve

$$\Sigma(Y_i - b_o - b_1X_i) = 0 \tag{8}$$

$$\Sigma(Y_i - b_o - b_1X_i)X_i = 0 \tag{9}$$

Rearranging the terms and collecting them into a computable form gives the following as solutions for b_o and b_1

$$b_1 = \frac{n\Sigma XY - (\Sigma X)(\Sigma Y)}{n\Sigma X^2 - (\Sigma X)^2} \tag{10}$$

$$b_o = (\Sigma Y - b_1\ \Sigma X)/n \tag{11}$$

(The subscripts have been eliminated since all n observations are used in the summations.) Substitution of Equation (11) into Equation (3) and rearranging terms gives

$$Y' = \bar{Y} + b_1 (X - \bar{X}) \tag{12}$$

If we subtract each side of Equation (12) from the observation (Y) itself we have

$$Y - Y' = Y - \bar{Y} - b_1 (X - \bar{X}) \tag{13}$$

Summation over all of the n observations yields

$$\Sigma(Y - Y') = \Sigma(Y - \bar{Y}) - b_1 \Sigma(X - \bar{X}) \tag{14}$$

Since both terms of the right-hand side equal zero, we have that the sum of the residuals (observation minus prediction) is equal to zero, i.e., the deviations are minimum.

Linear Regression, Precision

The precision of the regression line (and the validity of our original assumption) is determined from the identity:

$$Y_i - Y_i' = Y_i - \bar{Y} - (Y_i' - \bar{Y})$$

If we square both sides of the identity and sum over all observations it can be shown that

$$\Sigma(Y_i - \bar{Y})^2 = \Sigma(Y_i - Y_i')^2 + \Sigma(Y_i' - \bar{Y})^2 \tag{15}$$

and note that the left-hand side of Equation (15) is the sums of squares of deviations of the observations from the mean. The first term on the right-hand side is the sum of squares of the deviations of the observations from their predictions; and the second term is the sum of squares of the deviations of the predictions from the mean we can write Equation (15) in words as follows:

$$\begin{matrix}\text{Sum of squares} \\ \text{about the mean}\end{matrix} = \begin{matrix}\text{Sum of squares} \\ \text{about regression}\end{matrix} + \begin{matrix}\text{Sum of squares} \\ \text{due to regression}\end{matrix}$$

This shows that some of the variation can be ascribed to the regression line and some to the fact that the actual values do not all lie on the regression line. We assess the usefulness of the regression line as a predictor by comparing how much of the SS about the mean falls into the SS due to regression against the amount that falls into the SS about the regression. The ratio r^2 is computed as

$$r^2 = \frac{\text{SS due to regression}}{\text{SS about the mean}}$$

and we note that when $r^2 = 1$, we have no deviations of predictions from their observations; when $r^2 = 0$, we have that the regression equation is useless in its present form.

Multiple Linear Regression —

The usual situation encountered is not that of a response and one independent variable. In many cases it is known beforehand that a response is dependent upon several variables. We require information about the type of relationship (positive, inverse, curvilinear, etc.), the magnitude of the dependence, and the interactions of the independent variables with the response.

Let us assume that we have three independent variables, X_1, X_2, and X_3 and the response Y, and we have data from an experiment designed to insure independent estimates of the parameters. If we assume the model

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{1,2} X_1 X_2 + \beta_{1,3} X_1 X_3$$
$$+ \beta_{2,3} X_2 X_3 + \beta_{1,1} X_1^2 + \beta_{2,2} X_2^2 + \beta_{3,3} X_3^2 + \varepsilon$$

and obtain estimates b_i of the β_i as described previously. The solution is obtained by solving simultaneous linear equations which result from differentiating the Function S [Equation (5)] under our present assumptions. A statistical test is made for each of the parameters to determine whether the parameter is equal to zero (i.e., no effect) or not equal to zero.

The interpretation of the b_i and b_{ii} parameters is straightforward. The "interaction" parameters, b_{ij}, is testing the independence of the effect of the variables "i" and "j" upon the response. If it is found that a parameter b_{ij} is not equal to zero, it implies the effect is dependent upon the levels of the two variables.

PYROLYSIS-GAS LIQUID CHROMATOGRAPHY

The Varian Aerographs 1400 series gas chromatograph was used for this purpose. Selected samples of freeze-dried color bodies from dilute waste liquors were subjected to pyrolysis-gas liquid chromatography (GLC). The conditions were as follows:

Pyrolysis: Hamilton Multi-Purpose Sampling System
Furnace temp, 400°C
Oven zone temp, 240-245°C
Heated line temp, 240-260°C
Injector: 190-200°C
Column: 10 percent Carbowax 20M; 5 ft x 1/8 inch
Initial temp, 75°C
Final temp, 200°C
Rate, 4°/min
Detector: Hydrogen flame ionization
Temp, 275-285°C
Gas sources: Carrier gas: He at 75 ml/min
Hydrogen: Varian Aerograph Model 9652 Hydrogen Generator
Air: Cylinder
Sample size: Sample weights could not be kept constant due to differences in ash contents. Most of the samples were not weighed for this qualitative study.

Modular Construction

The Hamilton Multi-Purpose Sampling System consists of temperature control unit, a gas control unit, a furnace assembly, a heated line and miscellaneous parts and supply.

The temperature control unit supplies adjustable power to the Furnace Assembly and Heated Line. It also provides thermocouple meter read-out of temperature at two points in the Furnace Assembly and at one point in the Heated Line.

The gas control unit provides means for diverting carrier gas through the Furnace Assembly to flush sample vapors into the inlet of the gas chromatograph by way of the Heated Line and its terminal needle.

The Furnace Assembly includes a tubular Vycor chamber in which the sample is processed. This processing tube passes through three zones of Furnace Assembly:

(1) A room temperature zone, where the sample may be held while purging air from the system,

(2) a furnace zone, capable of 800°C, into which the sample is dropped for heating,

(3) an oven zone, which heats to 300°C for vapor holding. After passing through the oven, the processing tube connects directly with the heated line.

The Heated Line operates at temperatures up to 300°C and has only stainless steel in contact with the sample. It is quite flexible, to allow insertion of its terminal needle into the chromatograph inlet. According to the Hamilton manual the insulation on Heated Line should permit safe handling at high temperatures. Our experience showed, however, that the Line could not be handled with bare hands.

Sample Handling

Samples are usually contained in thin-wall quartz sample tubes during processing. One purpose of the sample tube is to facilitate determination of initial sample weight and weight of residuals after pyrolysis. Another purpose is to insure that all forms of sample — powders, liquids, etc. — drop into the furnace in an identical manner, to the same spot, and are exposed to identical conditions. The sample also protects the processing tube from direct contact with other than sample vapors, thus lengthening the time between cleanings.

The best method of retaining samples is to use small plugs of woven quartz fiber yarn or quartz wool.

Quartz tubes and loosely "wadded" quartz wool were fired in a muffle oven at 800°C until clean (usually 15 minutes were enough) and cooled in a desiccator. Sample tubes and quartz wool were handled with tweezers to avoid contamination by body oils. Samples were loaded in the tubes as follows:

(1) Sample tube was plugged on one side with the wadded quartz wool.

(2) The tube was held with clean tweezers and the solid sample was loaded through a small funnel made out of aluminum foil, solvent cleaned on the side that contacts the sample. The open end of the filled tube was then plugged with quartz wool as before. The plugs were dense enough to prevent the sample grains from falling.

(3) In case of low density powders, the open end of the sample tube was inverted on the sample and pushed, turned upright and tapped on the plugged end for the sample to fall in the tube. In some cases, clean needles were used to push the sample to the middle of the tube before plugging the open end.

(4) Care was taken to ensure that no grains were left on the outside of the sample tube.

(5) The liquid samples were injected with a microliter syringe onto the quartz packing, allowing capillary action to retain the sample.

Sample tubes (filled) were inserted into the processing tube through the sample port and the cap was screwed in (sample introduction knob was on "on" position and the gas flow had been adjusted to 75 ml/min with the help of flow balance adjust). The furnace assembly was tipped to drop the sample tube onto the quartz wool plug in the furnace zone, lowered back to horizontal position, latched in place and the GLC column oven linear temperature program and recorder chart were started.

SECTION VIII

REFERENCES

1. National Council of the Pulp & Paper Industry for Air and Stream Improvement (NCASI). Tech. Bull. No. 157, Dec. 1962.

2. Le Compte, A. R. Tappi. 49(12):121A, 1966.

3. Berger, H. F. and R. I. Brown. Tappi. 42(3):245, March 1959.

4. Smith, D. R. and H. F. Berger. Tappi. 51(10):37A, Oct. 1968.

5. Davis, C. L., Jr. Tappi. 52(11):2132, Nov. 1969.

6. Spruill, E. L. Water and Sewage Works. Industrial Waste Supplement. 118:15, 1971.

7. Information from Humphrey, J. E. Project Director, International Paper Company, Springhill, La.

8. Dence, C., *et al*. NCASI Tech. Bull. 239, 1970.

9. Dugal, H. S., *et al*. EPA Report No. EPA-R2-73-141, February 1973.

10. Swanson, J. W., H. S. Dugal, M. A. Buchanan, and E. E. Dickey. Effluent Color Characterization Before and After Stoichiometric Lime Treatment. Environ. Protection Agency, Washington, D.C. Publication No. EPA-R2-73-086. February 1973. 75 p.

11. Schachman, H. K. Reprint from Methods in Enzymology. Vol IV. Academic Press Inc., New York, N.Y., 1957.

12. Goldschmid, L. O. *In* Sarkanen and Ludwig's Lignins Occurrence, Formation, Structure and Reactions. New York, Wiley Interscience, 1971. p. 256-258.

13. Goring, D. A. I. Chromophore Seminar, Raleigh, N.C., April 1972.

14. Chervenka, C. H. A manual of Methods for the Ultracentrifuge. Beckman Instruments Inc., 1969. p. 42-55.

15. Ortiz, De Serra, and Schnitzen's Soil. Biol. BioChem. 5(3):281-286, 1973.

16. Supplied by Fleck, J. PhD Student. The Institute of Paper Chemistry, 1973.

17. Personal communication. Spruill, E. L., Supervisor, Environmental Control, Continental Can Co., Hodge, La.

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18. Standard Methods. American Public Health Association (APHA). 12th ed., 1965. p. 129.

19. Goldschmid, O. Anal. Chem. 26(9):1421, 1954.

20. Bauer, N. Determination of Density. In Weissberger's Technique of Organic Chemistry. Physical Methods. 2nd ed. Vol. 1. Part 1. Interscience, New York, 1949. p. 254-296.

21. Draper, N. R., and Smith, H., Applied Regression Analysis, John Wiley & Sons, New York, 1966.

SECTION IX

APPENDICES

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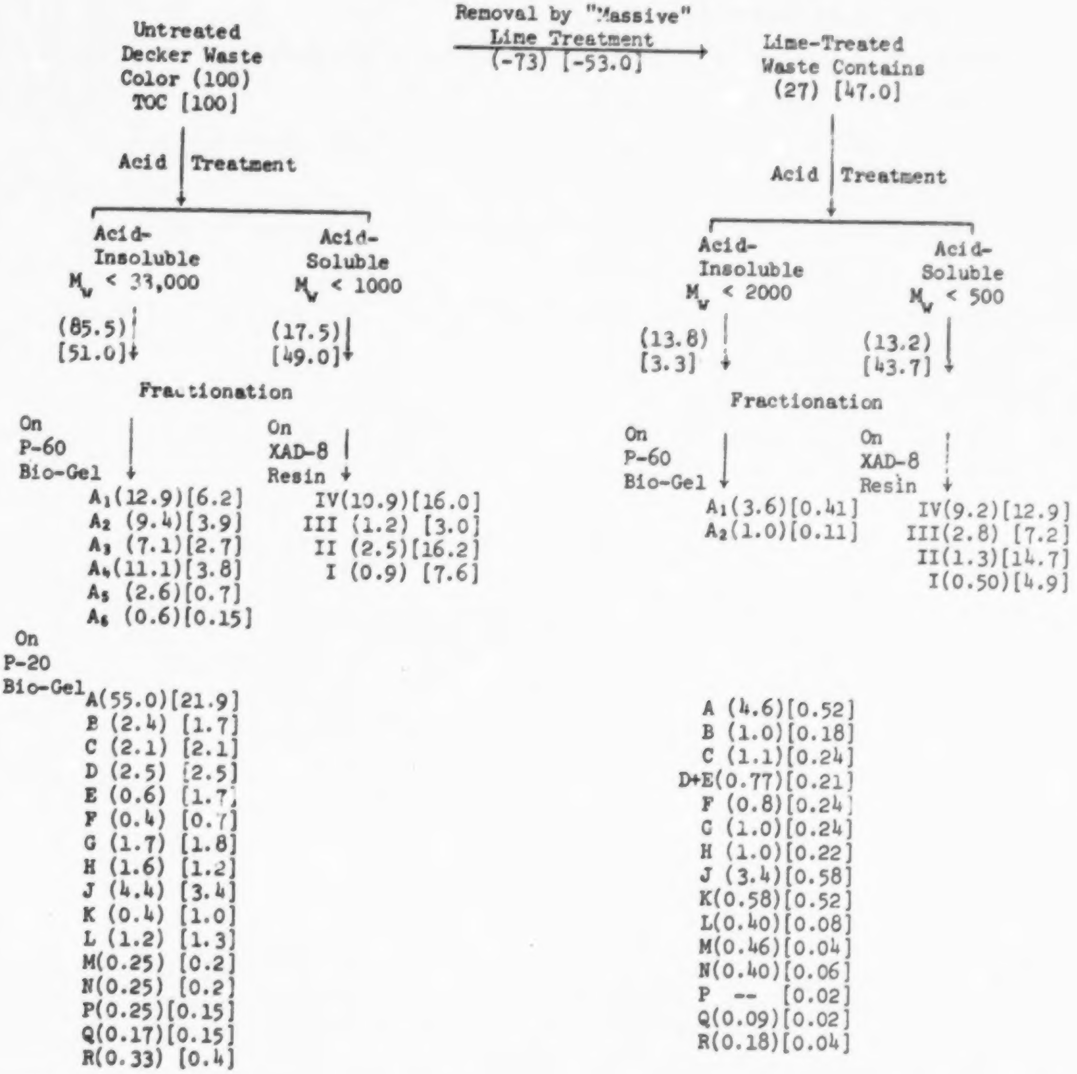
APPENDIX I

FRACTIONATION OF COLOR BODIES FROM IPCO'S KRAFT DECKER EFFLUENT
(Material Balance of Color and TOC)


Untreated Decker Waste Color (100) TOC [100]
Removal by "Massive" Lime Treatment
(-73) [-53.0]
Lime-Treated Waste Contains (27) [47.0]
Acid Treatment
Acid-Insoluble M_w < 33,000
Acid-Soluble M_w < 1000
(85.5) [51.0]
(17.5) [49.0]
Fractionation
On P-60 Bio-Gel
A_1(12.9)[6.2]
A_2 (9.4)[3.9]
A_3 (7.1)[2.7]
A_4(11.1)[3.8]
A_5 (2.6)[0.7]
A_6 (0.6)[0.15]
On XAD-8 Resin
IV(10.9)[16.0]
III (1.2) [3.0]
II (2.5)[16.2]
I (0.9) [7.6]
On P-20 Bio-Gel
A(55.0)[21.9]
B (2.4) [1.7]
C (2.1) [2.1]
D (2.5) [2.5]
E (0.6) [1.7]
F (0.4) [0.7]
G (1.7) [1.8]
H (1.6) [1.2]
J (4.4) [3.4]
K (0.4) [1.0]
L (1.2) [1.3]
M(0.25) [0.2]
N(0.25) [0.2]
P(0.25)[0.15]
Q(0.17)[0.15]
R(0.33) [0.4]
Acid Treatment
Acid-Insoluble M_w < 2000
Acid-Soluble M_w < 500
(13.8) [3.3]
(13.2) [43.7]
Fractionation
On P-60 Bio-Gel
A_1(3.6)[0.41]
A_2(1.0)[0.11]
On XAD-8 Resin
IV(9.2)[12.9]
III(2.8) [7.2]
II(1.3)[14.7]
I(0.50)[4.9]
A (4.6)[0.52]
B (1.0)[0.18]
C (1.1)[0.24]
D+E(0.77)[0.21]
F (0.8)[0.24]
G (1.0)[0.24]
H (1.0)[0.22]
J (3.4)[0.58]
K(0.58)[0.52]
L(0.40)[0.08]
M(0.46)[0.04]
N(0.40)[0.06]
P -- [0.02]
Q(0.09)[0.02]
R(0.18)[0.04]

M_w = apparent weight average molecular weight. Color values are shown in parentheses and TOC in brackets. Fraction 'A' from Bio-Gel P-2 was further fractionated on Bio-Gel P-60 column.

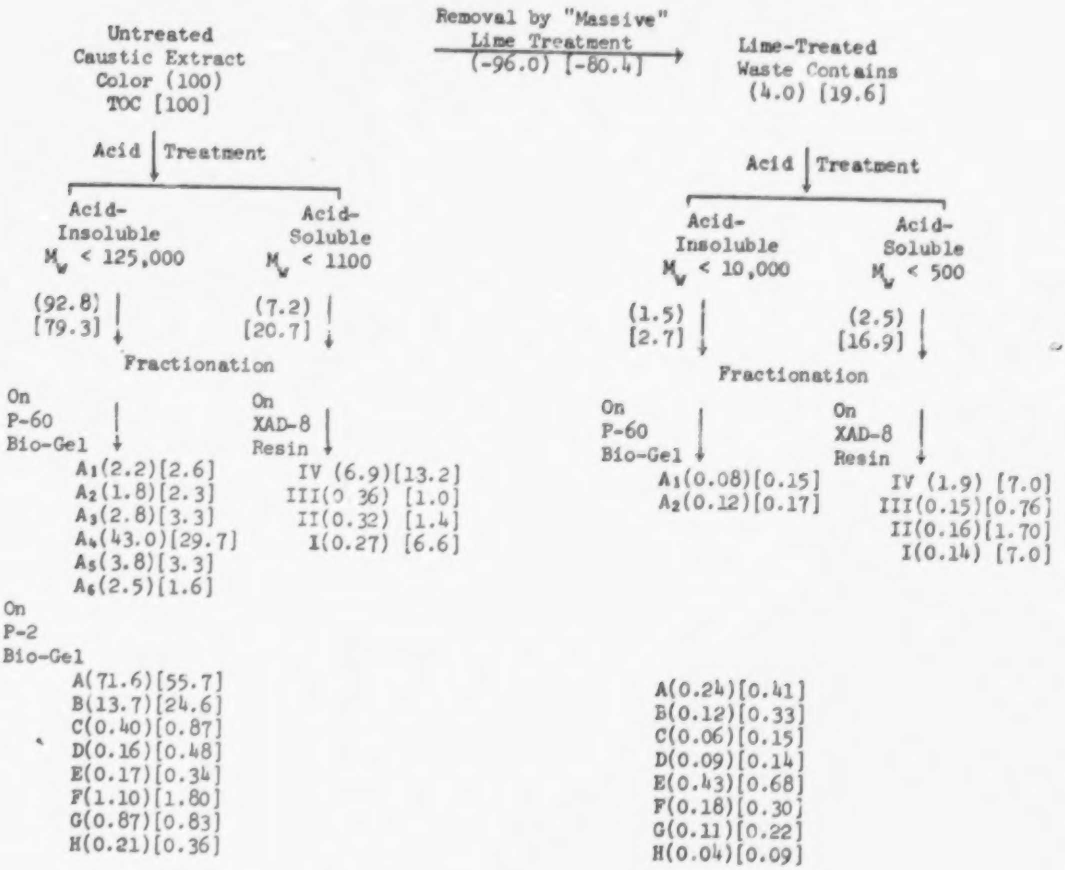
Appendix II. SUGAR ANALYSIS OF FREEZE-DRIED WASTES
(Basis o.d. Volatile Solids)

		Massive lime treatment				Stoichiometric lime treatment			
		Decker waste		Caustic extract		Decker waste		NSSC waste	
Sugars, %	Indulin -C	Untreated	Lime treated	Untreated	Lime treated	Untreated	Lime treated	Untreated	Lime Treated
Arabinose	0.37	0.04	<0.04	0.21	<0.04	0.22	<0.04	0.72	1.09
Galactose	1.69	0.60	<0.04	2.83	3.42	3.53	0.30	1.22	0.59
Glucose	0.02	2.37	<0.04	0.61	<0.04	0.66	0.91	0.25	0.67
Mannose	---	2.43	6.00	<0.04	<0.04	2.74	3.19	0.30	<0.04
Xylose	0.52	10.20	<0.04	0.95	<0.04	1.83	1.82	8.30	14.90
Total	2.60	16.41	6.00	4.60	3.42	8.98	6.22	10.79	17.25

APPENDIX III

FRACTIONATION OF COLOR BODIES FROM IPCO'S KRAFT BLEACH CAUSTIC EXTRACT

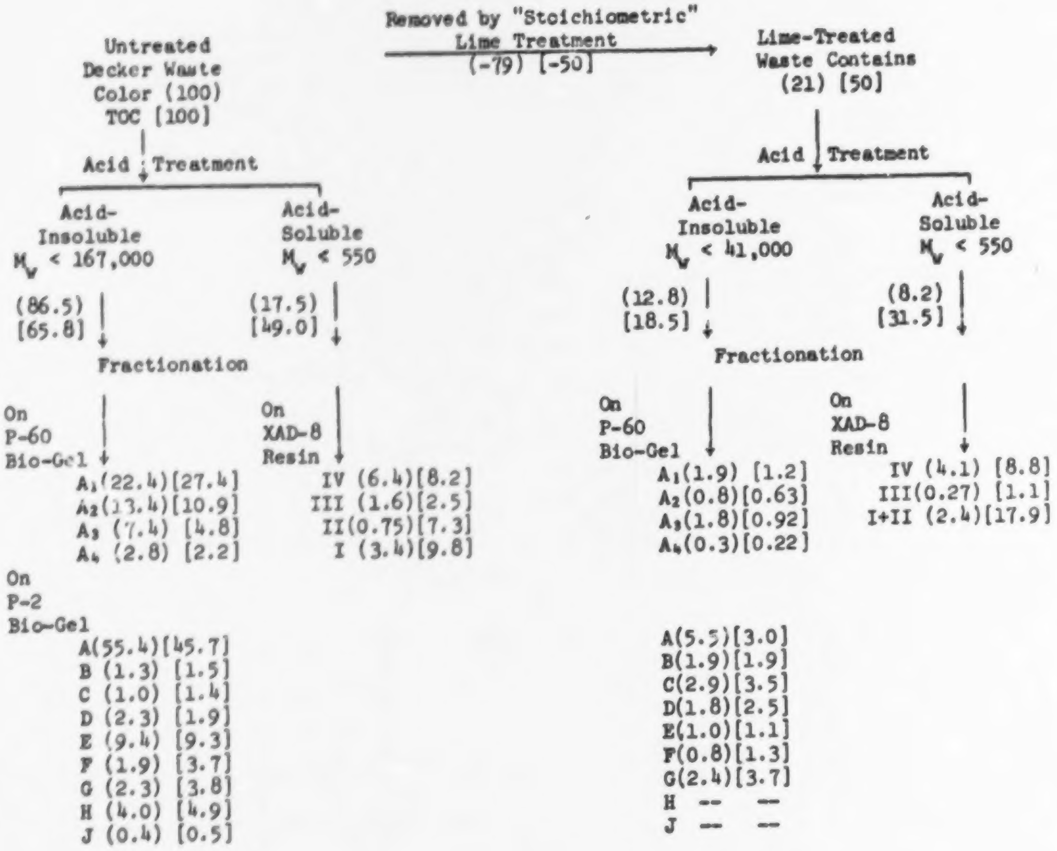
(Material Balance of Color and TOC)


Untreated
Caustic Extract
Color (100)
TOC [100]
Removal by "Massive"
Lime Treatment
(-96.0) [-80.4]
Lime-Treated
Waste Contains
(4.0) [19.6]
Acid Treatment
Acid-
Insoluble
M_w < 125,000
Acid-
Soluble
M_w < 1100
(92.8)
[79.3]
(7.2)
[20.7]
Fractionation
On
P-60
Bio-Gel
A_1(2.2)[2.6]
A_2(1.8)[2.3]
A_3(2.8)[3.3]
A_4(43.0)[29.7]
A_5(3.8)[3.3]
A_6(2.5)[1.6]
On
XAD-8
Resin
IV (6.9)[13.2]
III(0.36) [1.0]
II(0.32) [1.4]
I(0.27) [6.6]
On
P-2
Bio-Gel
A(71.6)[55.7]
B(13.7)[24.6]
C(0.40)[0.87]
D(0.16)[0.48]
E(0.17)[0.34]
F(1.10)[1.80]
G(0.87)[0.83]
H(0.21)[0.36]
Acid Treatment
Acid-
Insoluble
M_w < 10,000
Acid-
Soluble
M_w < 500
(1.5)
[2.7]
(2.5)
[16.9]
Fractionation
On
P-60
Bio-Gel
A_1(0.08)[0.15]
A_2(0.12)[0.17]
On
XAD-8
Resin
IV (1.9) [7.0]
III(0.15)[0.76]
II(0.16)[1.70]
I(0.14) [7.0]
A(0.24)[0.41]
B(0.12)[0.33]
C(0.06)[0.15]
D(0.09)[0.14]
E(0.43)[0.68]
F(0.18)[0.30]
G(0.11)[0.22]
H(0.04)[0.09]

M_w = apparent weight average molecular weight. Color values are shown in parentheses and TOC in brackets. Fraction "A" from Bio-Gel P-2 was further fractionated on Bio-Gel P-60 column.

APPENDIX IV

FRACTIONATION OF COLOR BODIES FROM CONCO'S KRAFT DECKER EFFLUENT
(Material Balance of Color and TOC)

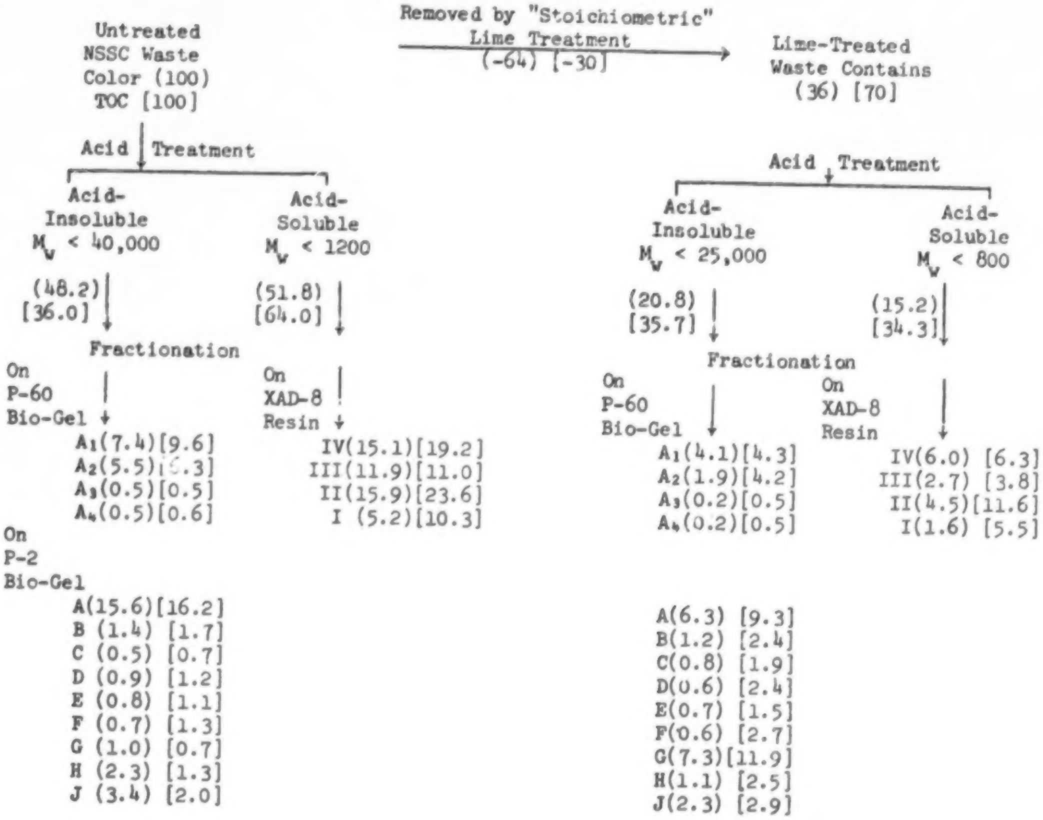

Removed by "Stoichiometric" Lime Treatment
(-79) [-50]
Untreated Decker Waste Color (100) TOC [100]
Acid Treatment
Acid-Insoluble M_w < 167,000
Acid-Soluble M_w < 550
(86.5) [65.8]
(17.5) [49.0]
Fractionation
On P-60 Bio-Gel
A_1(22.4)[27.4]
A_2(13.4)[10.9]
A_3 (7.4) [4.8]
A_4 (2.8) [2.2]
On XAD-8 Resin
IV (6.4)[8.2]
III (1.6)[2.5]
II(0.75)[7.3]
I (3.4)[9.8]
On P-2 Bio-Gel
A(55.4)[45.7]
B (1.3) [1.5]
C (1.0) [1.4]
D (2.3) [1.9]
E (9.4) [9.3]
F (1.9) [3.7]
G (2.3) [3.8]
H (4.0) [4.9]
J (0.4) [0.5]
Lime-Treated Waste Contains (21) [50]
Acid Treatment
Acid-Insoluble M_w < 41,000
Acid-Soluble M_w < 550
(12.8) [18.5]
(8.2) [31.5]
Fractionation
On P-60 Bio-Gel
A_1(1.9) [1.2]
A_2(0.8)[0.63]
A_3(1.8)[0.92]
A_4(0.3)[0.22]
On XAD-8 Resin
IV (4.1) [8.8]
III(0.27) [1.1]
I+II (2.4)[17.9]
A(5.5)[3.0]
B(1.9)[1.9]
C(2.9)[3.5]
D(1.8)[2.5]
E(1.0)[1.1]
F(0.8)[1.3]
G(2.4)[3.7]
H -- --
J -- --

M_w = apparent weight average molecular weight. Color values are shown in parentheses and TOC in brackets. Fraction "A" from Bio-Gel P-2 was further fractionated on Bio-Gel P-60 column.

APPENDIX V

FRACTIONATION OF COLOR BODIES FROM CONCO'S NSSC EFFLUENT

(Material Balance of Color and TOC)


Untreated
NSSC Waste
Color (100)
TOC [100]
Removed by "Stoichiometric"
Lime Treatment
(-64) [-30]
Lime-Treated
Waste Contains
(36) [70]
Acid Treatment
Acid-
Insoluble
M_w < 40,000
Acid-
Soluble
M_w < 1200
(48.2)
[36.0]
(51.8)
[64.0]
Fractionation
On
P-60
Bio-Gel
A_1(7.4)[9.6]
A_2(5.5)[6.3]
A_3(0.5)[0.5]
A_4(0.5)[0.6]
On
XAD-8
Resin
IV(15.1)[19.2]
III(11.9)[11.0]
II(15.9)[23.6]
I (5.2)[10.3]
On
P-2
Bio-Gel
A(15.6)[16.2]
B (1.4) [1.7]
C (0.5) [0.7]
D (0.9) [1.2]
E (0.8) [1.1]
F (0.7) [1.3]
G (1.0) [0.7]
H (2.3) [1.3]
J (3.4) [2.0]
Acid Treatment
Acid-
Insoluble
M_w < 25,000
Acid-
Soluble
M_w < 800
(20.8)
[35.7]
(15.2)
[34.3]
Fractionation
On
P-60
Bio-Gel
A_1(4.1)[4.3]
A_2(1.9)[4.2]
A_3(0.2)[0.5]
A_4(0.2)[0.5]
On
XAD-8
Resin
IV(6.0) [6.3]
III(2.7) [3.8]
II(4.5)[11.6]
I(1.6) [5.5]
A(6.3) [9.3]
B(1.2) [2.4]
C(0.8) [1.9]
D(0.6) [2.4]
E(0.7) [1.5]
F(0.6) [2.7]
G(7.3)[11.9]
H(1.1) [2.5]
J(2.3) [2.9]

M_w = Apparent weight average molecular weight. Color values are shown in parentheses and TOC in brackets. Fraction "A" from Bio-Gel P-2 was further fractionated on Bio-Gel P-60 column.

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